Supporting Information for

Catalyst-free Photoarylation of 2-Aryl-2*H*-indazole by Carbon-Iodine Bond Activation

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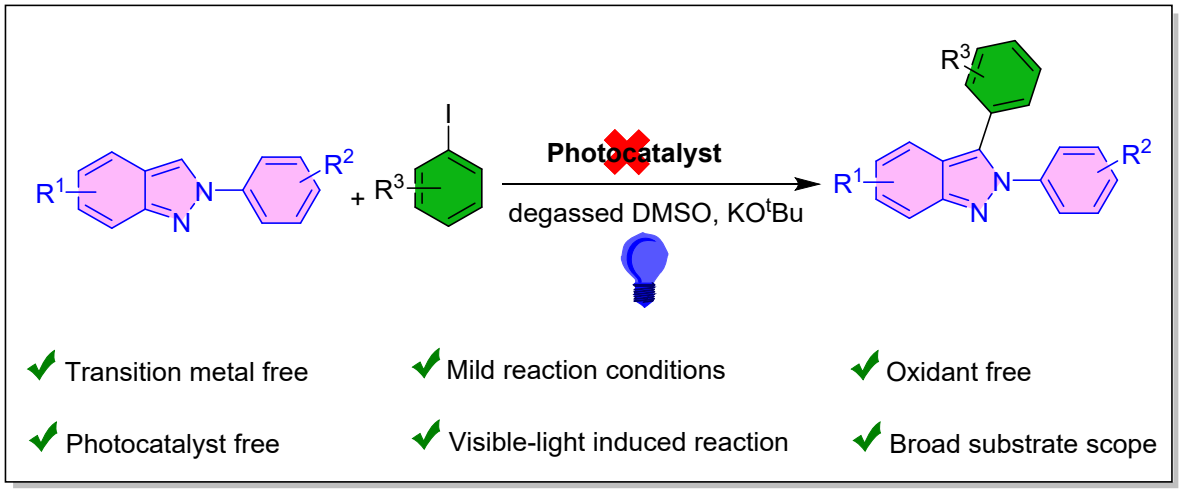
B. V. Subba Reddy*



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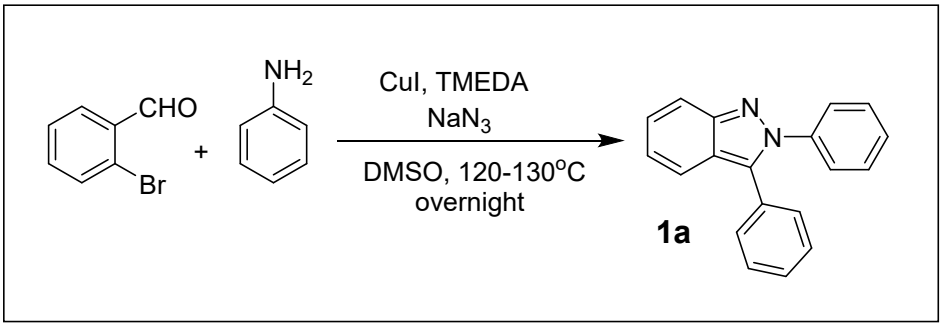
1. General information

All reactions were performed in oven-dried round bottom flasks and photoreaction vials, and the flasks were fitted with rubber septa and the reactions were conducted under a nitrogen atmosphere. Glass syringes were used to transfer solvents. Crude products were purified by column chromatography on silica gel 100-200 mesh. Thin layer chromatography (TLC) plates were visualized by exposure to ultraviolet light at 254 nm, and by exposure to iodine vapours and/or by exposure to methanolic acidic solution of *p*-anisaldehyde followed by heating (<1 min) on a hot plate (approx. 250 °C). Organic solutions were concentrated on rotary evaporator at 35–40 °C. Melting points (MP) were obtained on Buchi B-540. ^{1}H, ^{13}C (proton decoupled) and ^{19}F NMR spectra were recorded in $CDCl_3$ using 400 or 500 MHz (^{1}H), 101, 126 or 151 MHz (^{13}C) and 376, 377 or 471 MHz (^{19}F). Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra and HRMS were recorded on mass spectrometer by Electrospray ionization (ESI) techniques. Photochemical reactions were performed using Penn PhD Photoreactor M2 (Sigma-Aldrich).

2. General procedures for the synthesis of starting materials:



Scheme S1. Preparation of 2-phenyl-2*H*-indazole

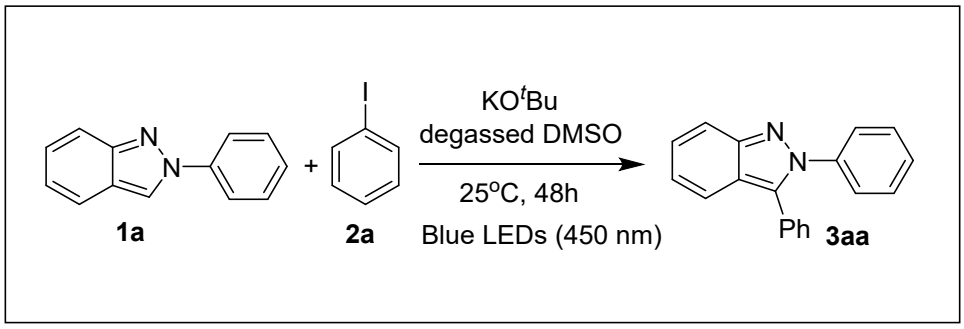
2-Phenyl-2*H*-indazole was prepared following a reported procedure.[1] In an oven-dried 25 mL round bottom flask, CuI (29 mg, 0.15 mmol), 2-bromobenzaldehyde (287 mg, 1.5 mmol), sodium azide (196 mg, 3.0 mmol), TMEDA (17 mg, 0.15 mmol) and anilines (1.8 mmol) were added to 5 mL of DMSO. The reaction mixture was heated to 120-130°C for overnight. The consumption of starting materials was confirmed by TLC and the reaction mixture was brought to room temperature. Later on, the mixture was poured into 50 mL of EtOAc and washed with water (3 × 25 mL), brine (2 × 25 mL), then dried over Na_2SO_4 and was passed through Celite. Evaporation of the solvent under reduced pressure provided the crude product, which was further purified by column chromatography (*n*-hexane: EtOAc = 10:1) to afford the final product **1a** as a yellow solid in 95% yield (276 mg).

Similarly, other substituted 2-aryl-2*H*-indazoles were prepared following the aforesaid procedure.

3. Photoreaction set-up:

Figure S1. Penn PhD Photoreactor M2 (Sigma-Aldrich)

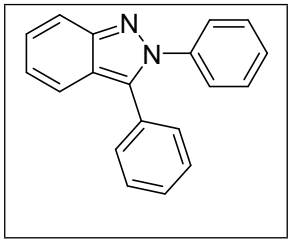
4. Experimental procedure for photoredox arylation and characterization of products:



Scheme S2. Photoredox arylation of 2-phenyl-2*H*-indazole

In a flame-dried reaction vial, potassium *tert*-butoxide (157 mg, 1.40 mmol) and 4 mL of dry degassed DMSO were taken under a nitrogen atmosphere. Then, the reaction tube was sealed with a rubber septum. Iodobenzene **2a** (286 mg, 156 µL, 1.40 mmol) was added to the reaction vial under a nitrogen atmosphere, and the reaction was stirred at room temperature for 30 min. Later, 2-phenyl-2*H*-indazole **1a** (90 mg, 0.46 mmol) were added to the reaction vial, and the reaction was stirred at room temperature using 450 nm blue LEDs as source of irradiation. The progress of the reaction was monitored by TLC and after completion of the reaction; it was extracted with ethyl acetate (20 mL). The combined organic layer was washed with water (3 × 10 mL) and dried over anhydrous Na_2SO_4. The organic layer was evaporated under reduced pressure, and the crude product was purified by column chromatography to give 2,3-diphenyl-2*H*-indazole **3aa** (89 mg, 71% yield).

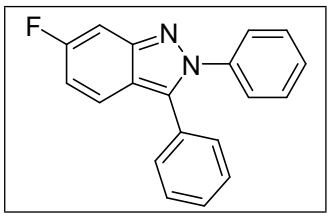
2,3-Diphenyl-2*H*-indazole (3aa):



Yield (89 mg, 71%), yellowish white solid, mp.104 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.72 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.47 – 7.35 (m, 11H), 7.15 (ddd, *J* = 8.5, 6.6, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 140.3, 135.5, 129.9, 129.7, 129.0, 128.8, 128.3, 128.3, 127.0, 126.1, 122.5, 121.8, 120.6, 117.8. HRMS (*ESI Orbitrap*) calcd for $C_{19}H_{14}N_2$ $[M+H]^+$: 271.1235 Found: 271.1277.

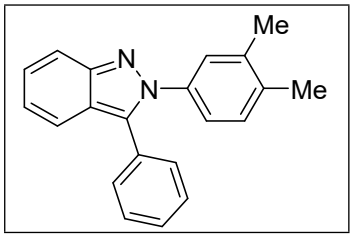
Similarly, other photoarylated products were also prepared by following the procedure mentioned above.

6-Fluoro-2,3-diphenyl-2*H*-indazole (3ba):



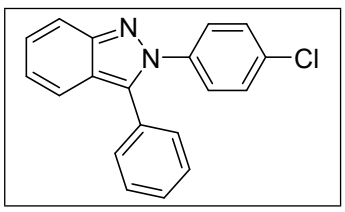
Yield (90 mg, 68%), white solid, mp.108 °C,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.40 (m, 8H), 7.34 – 7.28 (m, 3H), 7.17 (t, *J* = 8.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (d, J_{C-F} = 240.5 Hz), 146.4, 140.1, 135.7, 135.6, 129.6, 129.5, 129.0 (d, J_{C-F} = 17.4 Hz), 128.5 (d, J_{C-F} = 1.9 Hz), 125.9, 121.1 (d, J_{C-F} = 11.3 Hz), 119.9 (d, J_{C-F} = 9.7 Hz), 118.6 (d, J_{C-F} = 28.9 Hz), 102.9 (d, J_{C-F} = 24.4 Hz).^{19}F NMR (376 MHz, $CDCl_3$) δ -119.22. HRMS (*ESI Orbitrap*) calcd for $C_{19}H_{14}N_2F$ $[M+H]^+$: 289.1141 Found: 289.1183.

2-(3,4-Dimethylphenyl)-3-phenyl-2*H*-indazole (3ca):



Yield (85 mg, 62%), white solid, mp.103 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.33 (m, 7H), 7.17 – 7.11 (m, 1H), 7.04 (dd, *J* = 25.8, 7.8 Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 138.0, 137.7, 136.9, 135.2, 130.1, 129.8, 129.7, 128.7, 128.21, 126.7, 126.8, 123.2, 122.3, 121.7, 120.5, 117.7, 19.8, 19.5. HRMS (*ESI Orbitrap*) calcd for $C_{21}H_{18}N_2$ $[M+H]^+$: 299.1543 Found: 299.1540.

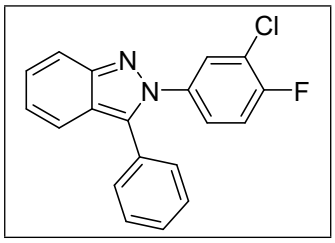
2-(4-Chlorophenyl)-3-phenyl-2*H*-indazole (3da):



Yield (94 mg, 67%), white solid, mp.113 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.45 – 7.32 (m, 10H), 7.17 – 7.11 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 138.8, 135.5, 134.1, 129.7, 129.7, 129.2, 129.0, 128.6, 127.3, 127.1,

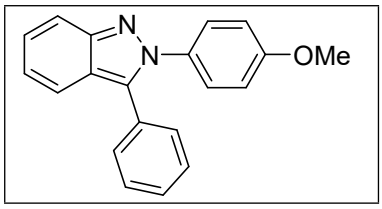
122.8, 121.9, 120.5, 117.7. HRMS (*ESI Orbitrap*) calcd for $C_{19}H_{13}ClN_2$ $[M+H]^+$: 305.0840 Found: 305.0838.

2-(3-Chloro-4-fluorophenyl)-3-phenyl-2*H*-indazole (3ea):



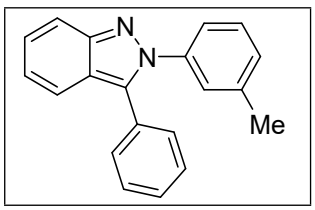
Yield (96 mg, 65%), yellow solid, mp. 121 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.69 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.65 (dd, *J* = 6.5, 2.6 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.41 – 7.34 (m, 3H), 7.22 (ddd, *J* = 8.8, 4.1, 2.6 Hz, 1H), 7.15 (ddd, *J* = 8.5, 6.6, 0.7 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 156.4, 149.2, 136.3 (d, J_{C-F} = 113.0 Hz), 129.7, 129.4, 129.1, 128.8, 128.3, 127.5, 125.6 (d, J_{C-F} = 7.5 Hz), 122.9, 121.8, 121.7, 120.5, 117.7, 116.7 (d, J_{C-F} = 22.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.03. HRMS (*ESI Orbitrap*) calcd for $C_{19}H_{12}ClFN_2$ $[M+H]^+$: 323.0746 Found: 323.0742.

2-(4-Methoxyphenyl)-3-phenyl-2*H*-indazole (3fa):



Yield (101 mg, 73%), brown solid, mp.126 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.37 (dt, *J* = 13.9, 7.1 Hz, 8H), 7.17 – 7.01 (m, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 148.8, 135.3, 133.4, 130.0, 129.7, 128.8, 128.24, 127.2, 126.9, 122.4, 121.6, 120.5, 117.7, 114.2, 55.5. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{17}ON_2$ $[M+H]^+$: 301.1335 Found: 301.1334.

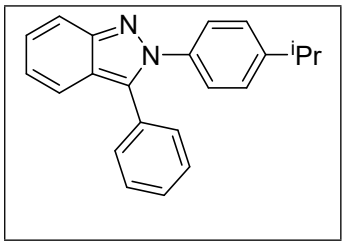
3-Phenyl-2-(*m*-tolyl)-2*H*-indazole (3ga):



Yield (93 mg, 71%), white solid, mp.59 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 32.3, 8.2 Hz, 2H), 7.38 (s, 7H), 7.24 – 7.06 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 140.17, 139.3, 135.4, 130.0, 129.7, 129.1, 128.7, 128.6, 128.3, 127.0, 126.6, 123.1,

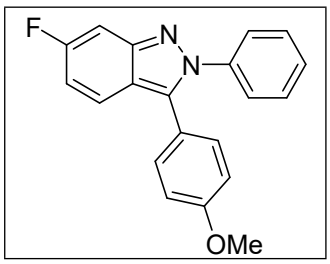
122.5, 121.7, 120.6, 117.8, 21.4. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{17}N_2$ $[M+H]^+$: 285.1386 Found: 285.1384.

2-(4-Isopropylphenyl)-3-phenyl-2*H*-indazole (3ha):



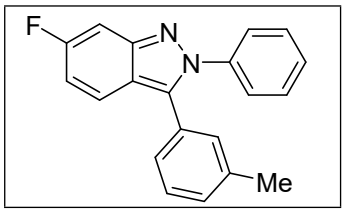
Yield (96 mg, 67%), white solid, mp.112 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.33 (m, 8H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.11 (m, 1H), 2.94 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 148.9, 138.0, 135.3, 130.1, 129.7, 128.7, 128.2, 127.0, 126.9, 125.8, 122.4, 121.7, 120.5, 117.7, 33.8, 23.9. HRMS (*ESI Orbitrap*) calcd for $C_{22}H_{21}N_2$ $[M+H]^+$: 313.1699 Found: 313.1696.

6-Fluoro-3-(4-methoxyphenyl)-2-phenyl-2*H*-indazole (3bb):



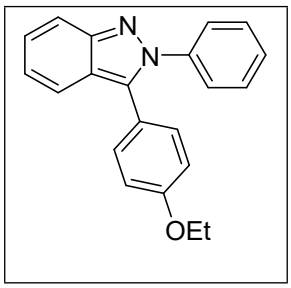
Yield (111 mg, 76%), white solid, mp.100 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.6, 4.1 Hz, 1H), 7.47 – 7.36 (m, 6H), 7.23 (s, 2H), 7.21 – 7.12 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 159.7, 158.9 (d, $J_{C\text{-}F}$ = 240.2 Hz), 146.4, 140.2, 135.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 130.8, 129.1, 128.3, 125.9, 121.9, 120.9 (d, $J_{C\text{-}F}$ = 11.3 Hz), 119.8 (d, $J_{C\text{-}F}$ = 9.6 Hz), 118.6 (d, $J_{C\text{-}F}$ = 29.0 Hz), 114.4, 103.0 (d, $J_{C\text{-}F}$ = 24.4 Hz), 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.67. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{16}ON_2F$ $[M+H]^+$: 319.1241 Found: 319.1238.

6-Fluoro-2-phenyl-3-(*m*-tolyl)-2*H*-indazole (3bc):



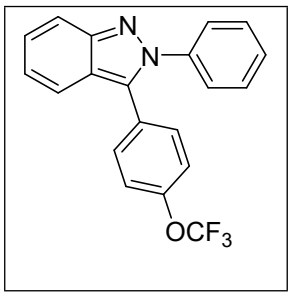
Yield (97 mg, 70%), white solid, mp.108 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 9.2, 4.6 Hz, 1H), 7.40 (dd, *J* = 14.8, 4.9 Hz, 5H), 7.32 – 7.23 (m, 2H), 7.16 (dd, *J* = 14.7, 4.8 Hz, 3H), 7.06 (d, *J* = 7.4 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (d, J_{C-F} = 240.4 Hz), 146.4, 140.2, 138.7, 135.8 (d, J_{C-F} = 8.5 Hz), 130.0, 129.5, 129.3, 129.0, 128.7, 128.4, 126.7, 125.9, 121.1 (d, J_{C-F} = 11.1 Hz), 119.9 (d, J_{C-F} = 9.6 Hz), 118.6 (d, J_{C-F} = 29.0 Hz), 103.0 (d, J_{C-F} = 24.4 Hz), 21.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -119.40. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{16}N_2F$ $[M+H]^+$: 303.1292 Found: 303.1290.

3-(4-Ethoxyphenyl)-2-phenyl-2*H*-indazole (3ad):



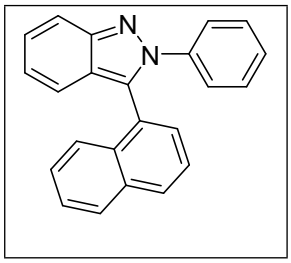
Yield (95 mg, 66%), white solid, mp.250 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 43.5, 8.6 Hz, 2H), 7.57 – 7.26 (m, 8H), 7.15 – 7.09 (m, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 4.06 (dd, *J* = 13.3, 6.5 Hz, 2H), 1.44 (t, *J* = 6.7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 149.0, 140.4, 135.5, 131.0, 129.0, 128.2, 127.0, 126.0, 122.19, 122.0, 121.6, 120.7, 117.7, 114.8, 63.5, 14.8. HRMS (*ESI Orbitrap*) calcd for $C_{21}H_{19}ON_2$ $[M+H]^+$: 315.1497 Found: 315.1510.

2-Phenyl-3-(4-(trifluoromethoxy)phenyl)-2*H*-indazole (3ae):



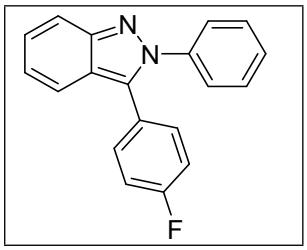
Yield (109 mg, 67%), white gummy solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.26 (m, 8H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.04 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 149.2, 139.0, 133.9, 132.4, 131.1, 128.3, 127.5, 127.4, 127.4, 123.2, 122.5, 122.0, 121.3, 120.4 (q, J_{C-F} = 257.8 Hz), 120.1, 117.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.72. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{14}ON_2F_3$ $[M+H]^+$: 355.1058 Found: 355.1058.

3-(Naphthalen-1-yl)-2-phenyl-2*H*-indazole (3af):



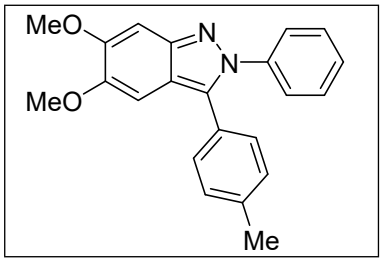
Yield (84 mg, 57%), yellow solid, mp.154 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.2, 4.1 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.42 – 7.34 (m, 6H), 7.24 – 7.20 (m, 3H), 7.10 – 7.02 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 140.3, 134.0, 133.8, 132.1, 129.7, 129.5, 128.9, 128.5, 128.0, 127.7, 127.1, 126.9, 126.4, 125.7, 125.4, 125.1, 123.4, 122.3, 120.9, 117.9. HRMS (*ESI Orbitrap*) calcd for $C_{23}H_{17}N_2$ $[M+H]^+$: 321.1392 Found: 321.1394.

3-(4-Fluorophenyl)-2-phenyl-2*H*-indazole (3ag):



Yield (95 mg, 72%), white solid, mp.147 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.67 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.45 – 7.37 (m, 6H), 7.36 – 7.31 (m, 2H), 7.16 (ddd, *J* = 8.5, 6.6, 0.8 Hz, 1H), 7.13 – 7.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, J_{C-F} = 249.3 Hz), 145.0, 140.1, 134.4, 131.5 (d, J_{C-F} = 8.2 Hz), 129.1, 128.4, 127.1, 126.0, 122.7, 121.7, 120.2, 117.9, 116.0 (d, J_{C-F} = 21.8 Hz).^{19}F NMR (377 MHz, $CDCl_3$) δ -112.32. HRMS (*ESI Orbitrap*) calcd for $C_{19}H_{14}N_2F$ $[M+H]^+$: 289.1135 Found: 289.1133.

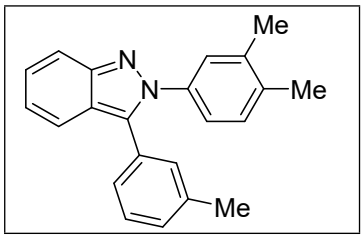
5,6-Dimethoxy-2-phenyl-3-(*p*-tolyl)-2*H*-indazole (3ih):



Yield (111 mg, 70%), white solid, mp.182 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 5H), 7.25 – 7.19 (m, 4H), 7.06 (s, 1H), 6.87 (s, 1H), 3.99 (s, 3H), 3.90 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 148.6, 145.6, 140.4, 138.1, 134.5, 129.6, 129.4, 128.9,

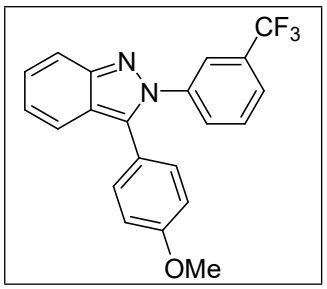
127.6, 127.4, 125.7, 116.2, 97.2, 95.7, 56.0, 21.4. HRMS (*ESI Orbitrap*) calcd for $C_{22}H_{21}O_2N_2$ $[M+H]^+$: 345.1603 Found: 345.1600.

2-(3,4-Dimethylphenyl)-3-(*m*-tolyl)-2*H*-indazole (3cc):



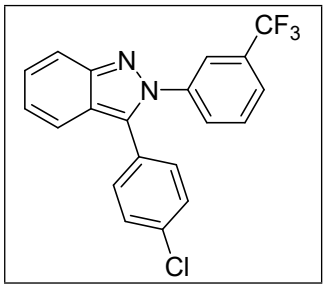
Yield (93 mg, 65%), yellowish white solid, mp.131 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.72 (s, 1H), 7.37 – 7.31 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.14 – 7.11 (m, 1H), 7.08 (dd, *J* = 11.4, 7.9 Hz, 2H), 7.00 (dd, *J* = 8.0, 2.1 Hz, 1H), 2.36 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 138.4, 138.0, 137.6, 136.8, 135.4, 130.2, 130.0, 129.8, 129.0, 128.6, 126.9, 126.8, 123.2, 122.2, 121.7, 120.6, 117.7, 21.5, 19.8, 19.5. HRMS (*ESI Orbitrap*) calcd for $C_{22}H_{21}N_2$ $[M+H]^+$: 313.1699 Found: 313.1696.

3-(4-Methoxyphenyl)-2-(3-(trifluoromethyl)phenyl)-2*H*-indazole (3jb):



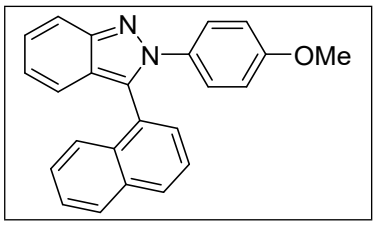
Yield (118 mg,70%), white solid, mp. 116 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.42 – 7.33 (m, 1H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.14 (dd, *J* = 8.0, 7.0 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 149.3, 140.8, 135.7, 131.7 (q, J_{C-F} = 33.0 Hz), 131.0, 129.5, 129.0, 127.5, 124.7 (q, J_{C-F} = 3.5 Hz), 123.0 (q, J_{C-F} = 3.7 Hz), 120.7 (q, J_{C-F} = 272.5 Hz), 121.9, 121.6, 120.7, 117.7, 114.6, 55.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.81. HRMS (*ESI Orbitrap*) calcd for $C_{21}H_{16}ON_2F_3$ $[M+H]^+$: 369.1209 Found: 369.1205.

3-(4-Chlorophenyl)-2-(3-(trifluoromethyl)phenyl)-2*H*-indazole (3jk):



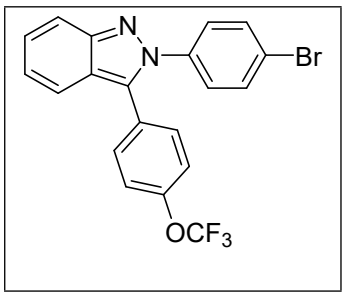
Yield (113 mg, 66%), white solid, mp.110 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.44 – 7.37 (m, 3H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.18 (dd, *J* = 8.0, 7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 140.5, 135.0, 134.4, 132.0 (d, J_{C-F} = 33.2 Hz), 130.9, 129.7, 129.4, 129.0, 127.9, 126.1 (d, J_{C-F} = 272.8 Hz), 125.1 (q, J_{C-F} = 3.3 Hz), 123.0 (q, J_{C-F} = 3.8 Hz), 121.4, 120.2, 118.0. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.84. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{12}ClN_2F_3$ $[M+H]^+$: 373.0709 Found: 373.0710.

2-(4-Methoxyphenyl)-3-(naphthalen-1-yl)-2*H*-indazole (3ff):



Yield (100 mg, 62%), yellowish white solid, mp.152 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.89 – 7.76 (m, 5H), 7.56 – 7.51 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 3H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.20 – 7.12 (m, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 148.9, 135.2, 133.4, 133.3, 132.8, 129.0, 128.4, 128.3, 127.8, 127.5, 127.2, 127.0, 126.9, 126.8, 126.7, 122.5, 121.9, 120.5, 117.8, 114.2, 55.5. HRMS (*ESI Orbitrap*) calcd for $C_{24}H_{19}ON_2$ $[M+H]^+$: 351.1492 Found: 351.1487.

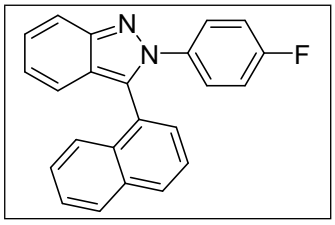
2-(4-Bromophenyl)-3-(4-(trifluoromethoxy)phenyl)-2*H*-indazole (3ke):



Yield (135 mg, 68%), yellow gummy solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.42 – 7.36 (m, 3H), 7.34 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.17 (ddd, *J* = 8.4, 6.7, 0.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0,

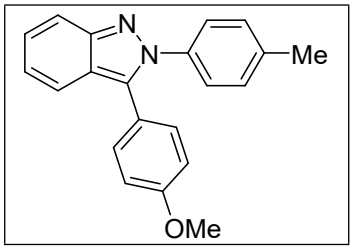
140.0, 133.9, 131.1, 129.2, 128.6, 127.2, 126.1, 124.0, 121.8, 120.5 (q, J_{C-F} = 257.9 Hz), 119.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.70. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{13}ON_2F_3Br$ $[M+H]^+$: 433.0163 Found: 433.0162.

2-(4-Fluorophenyl)-3-(naphthalen-1-yl)-2*H*-indazole (3lf):



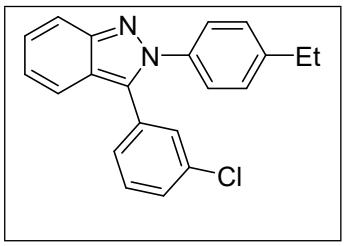
Yield (98 mg, 63%), yellowish white solid, mp.135 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 7.9 Hz, 2H), 7.86 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.62 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.38 (m, 6H), 7.08 (ddd, *J* = 8.5, 6.5, 0.8 Hz, 1H), 6.94 – 6.87 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9 (d, J_{C-F} = 248.5 Hz), 148.9, 136.4, 134.1, 133.8, 132.0, 129.7 (d, J_{C-F} = 7.6 Hz), 128.5, 127.4, 127.2, 127.0, 126.8 (d, J_{C-F} = 8.6 Hz), 126.4, 125.5, 125.3, 123.4, 122.5, 120.8, 117.8, 115.8 (d, J_{C-F} = 23.0 Hz).^{19}F NMR (377 MHz, $CDCl_3$) δ -113.17. HRMS (*ESI Orbitrap*) calcd for $C_{23}H_{16}N_2F$ $[M+H]^+$: 339.1290 Found: 339.1289.

3-(4-Methoxyphenyl)-2-(*p*-tolyl)-2*H*-indazole (3mb):



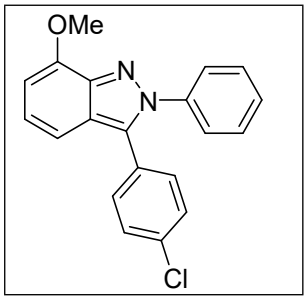
Yield (101 mg, 70%), white solid, mp.140 °C,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.38 (q, *J* = 9.0 Hz, 3H), 7.27 (d, *J* = 9.9 Hz, 2H), 7.16 – 7.09 (m, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 3.86 (s, 3H), 1.25 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 149.1, 138.9, 134.0, 131.0, 129.2, 127.3, 127.1, 127.0, 122.5, 121.9, 121.7, 120.6, 117.7, 114.5, 55.4, 29.7. HRMS (*ESI Orbitrap*) calcd for $C_{21}H_{19}N_2O$ $[M+H]^+$: 315.1497 Found: 315.1502.

3-(3-Chlorophenyl)-2-(4-ethylphenyl)-2*H*-indazole (3nl):



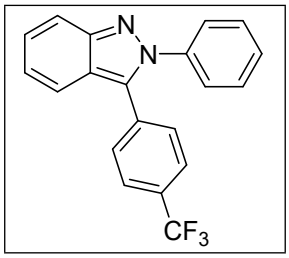
Yield (113 mg, 74%), white solid, mp.125 °C,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.70 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.41 (t, *J* = 1.6 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.36 – 7.28 (m, 4H), 7.24 – 7.21 (m, 2H), 7.20 – 7.14 (m, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 144.9, 137.6, 134.7, 133.6, 131.8, 130.0, 129.5, 128.6, 128.4, 127.9, 127.0, 125.8, 122.9, 121.8, 120.1, 117.9, 28.5, 15.4. HRMS (*ESI Orbitrap*) calcd for $C_{21}H_{18}N_2Cl$ $[M+H]^+$: 333.1159 Found: 333.1151.

3-(4-Chlorophenyl)-7-methoxy-2-phenyl-2*H*-indazole (3ok):



Yield (97 mg, 63%), white solid, mp.116 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.37 (dd, *J* = 7.8, 6.3 Hz, 5H), 7.29 (s, 1H), 7.24 (m, 2H), 7.11 – 7.05 (m, 1H), 6.64 (d, *J* = 7.3 Hz, 1H), 4.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 142.6, 140.0, 134.4, 134.3, 130.9, 129.1, 129.0, 128.5, 128.4, 126.3, 123.6, 123.3, 112.0, 103.4, 55.5. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{16}N_2OCl$ $[M+H]^+$: 335.0951 Found: 335.0935.

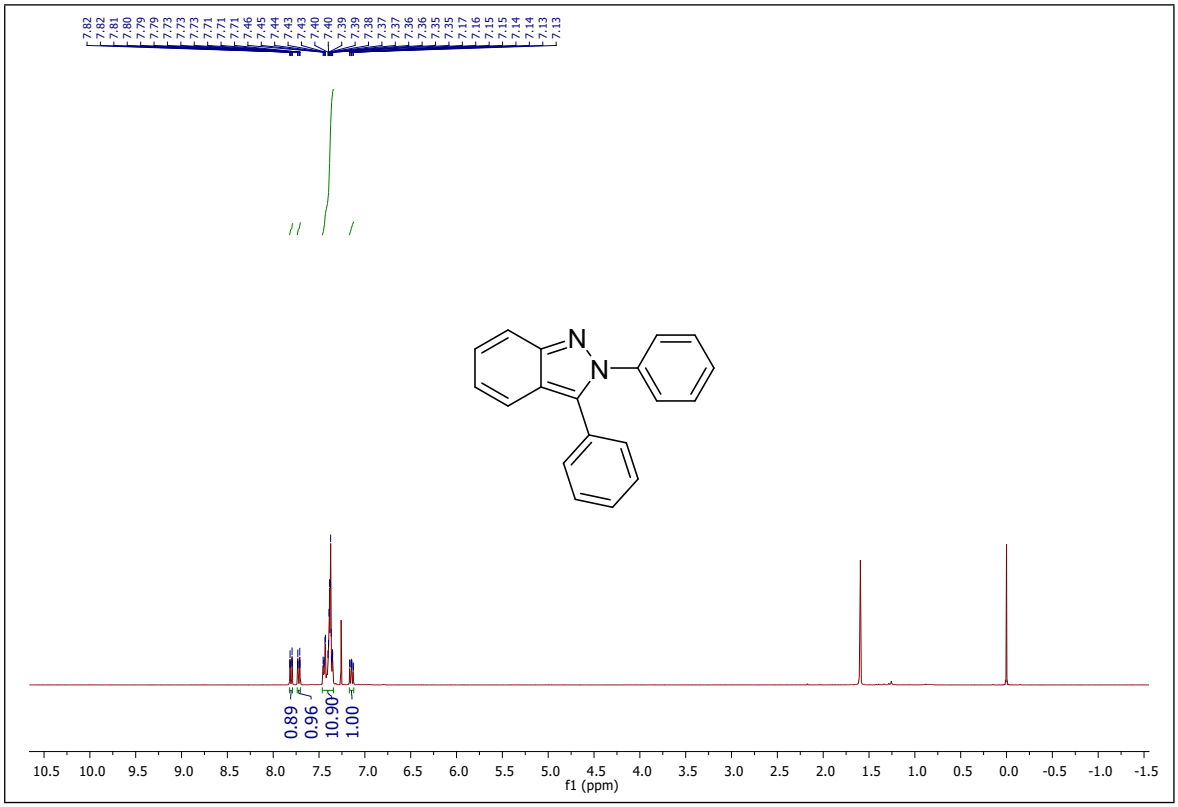
2-Phenyl-3-(4-(trifluoromethyl)phenyl)-2*H*-indazole (3ao):



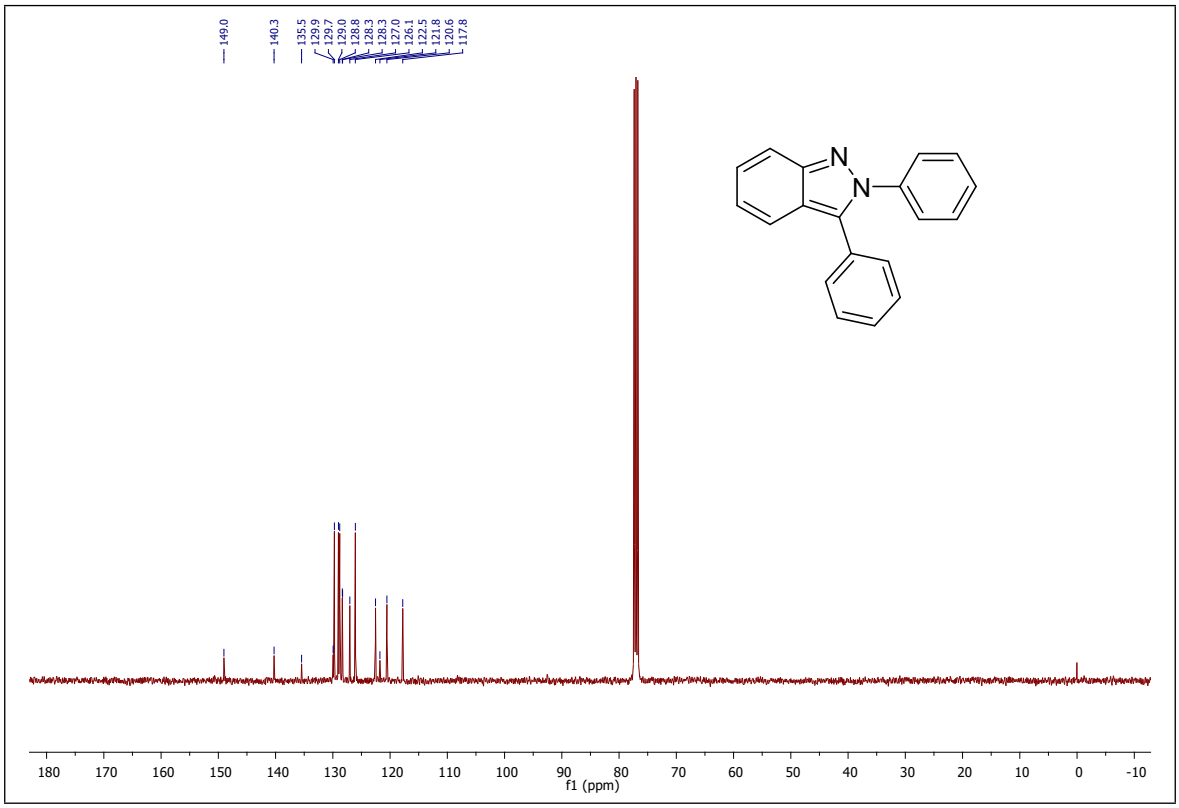
Yield (107 mg, 69%), white solid, mp.119 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 8.8, 0.8 Hz, 1H), 7.71 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 (m, 5H), 7.41 – 7.36 (m, 1H), 7.20 (ddd, *J* = 8.5, 6.6, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 139.9, 133.7, 133.6, 130.2 (q, *J* = 32.7 Hz), 129.3, 128.7, 127.2, 126.1, 125.8 (d, *J* = 3.4 Hz), 123.9 (q, *J* = 272.4 Hz), 123.3, 122.6, 119.9, 118.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.68. HRMS (*ESI Orbitrap*) calcd for $C_{20}H_{14}N_2F_3$ $[M+H]^+$: 339.1109 Found: 339.1114.

5. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of products:

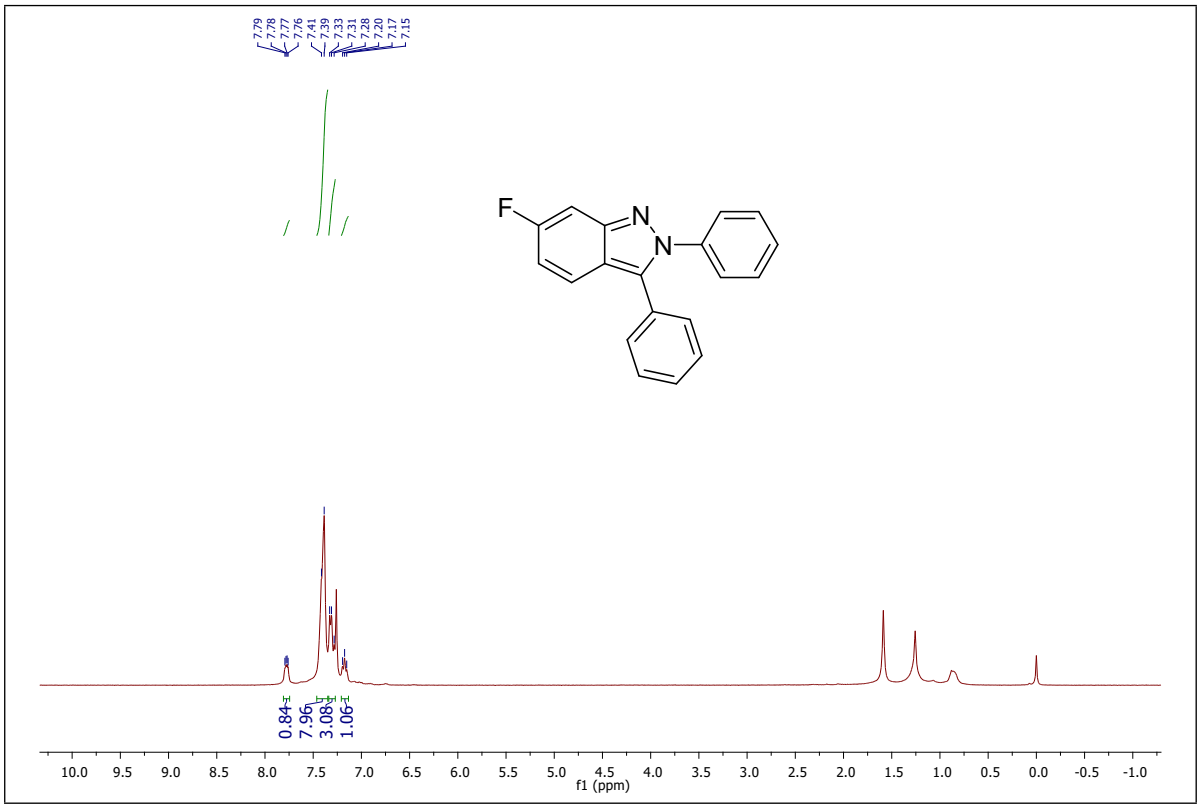
^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$):



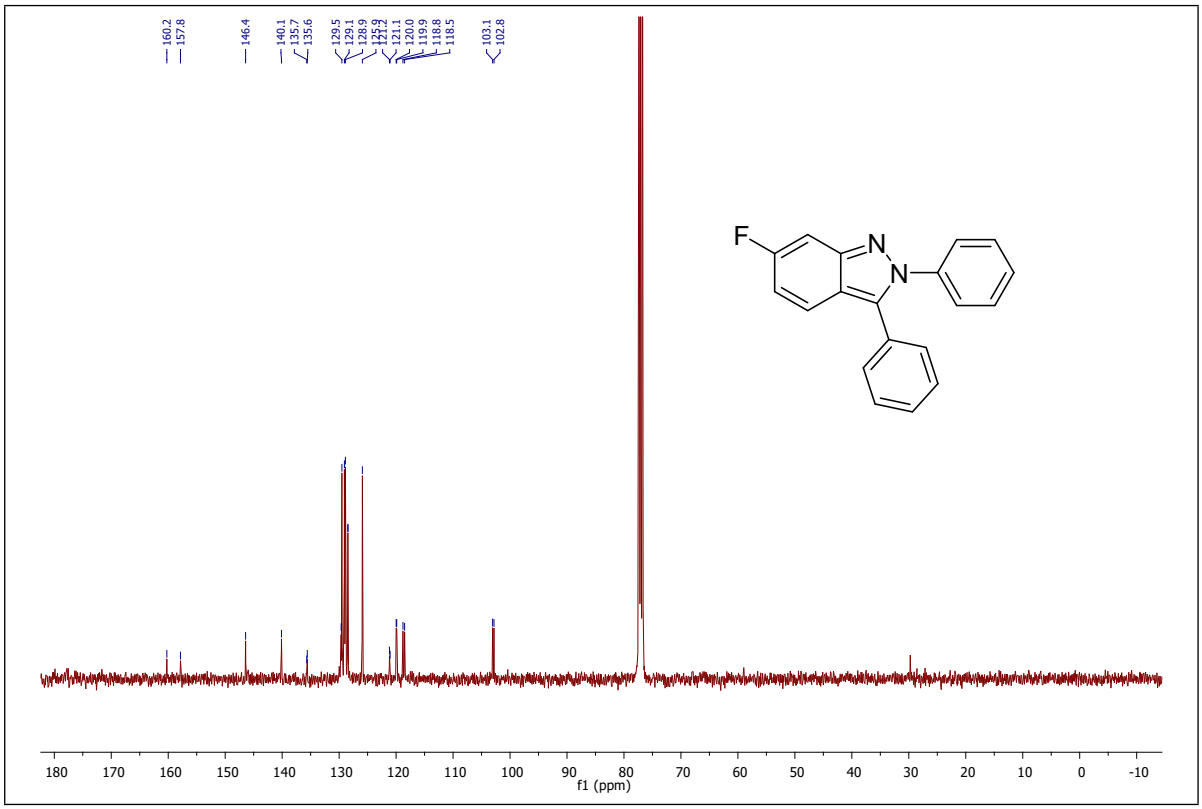
^{13}C NMR spectrum of **3aa** (101 MHz, $CDCl_3$):



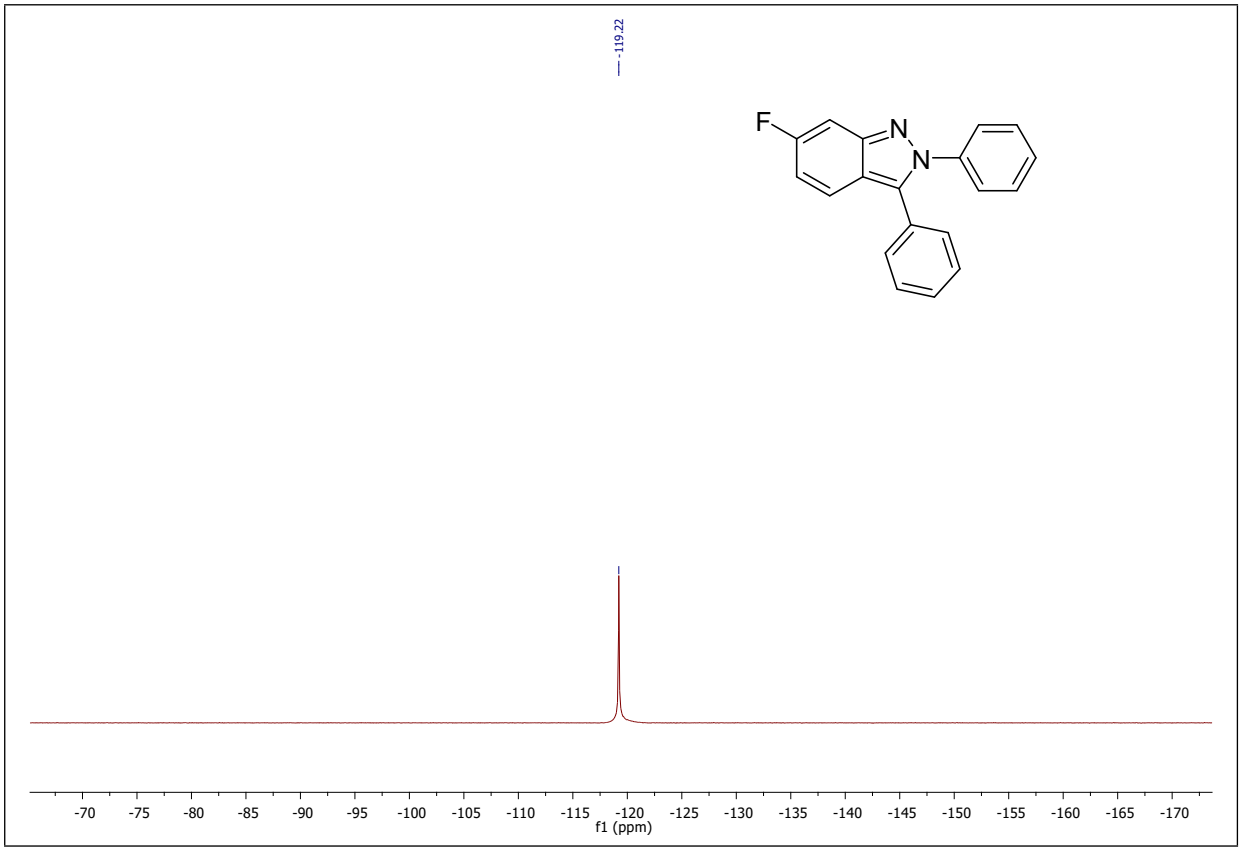
^{1}H NMR spectrum of **3ba** (400 MHz, $CDCl_3$):



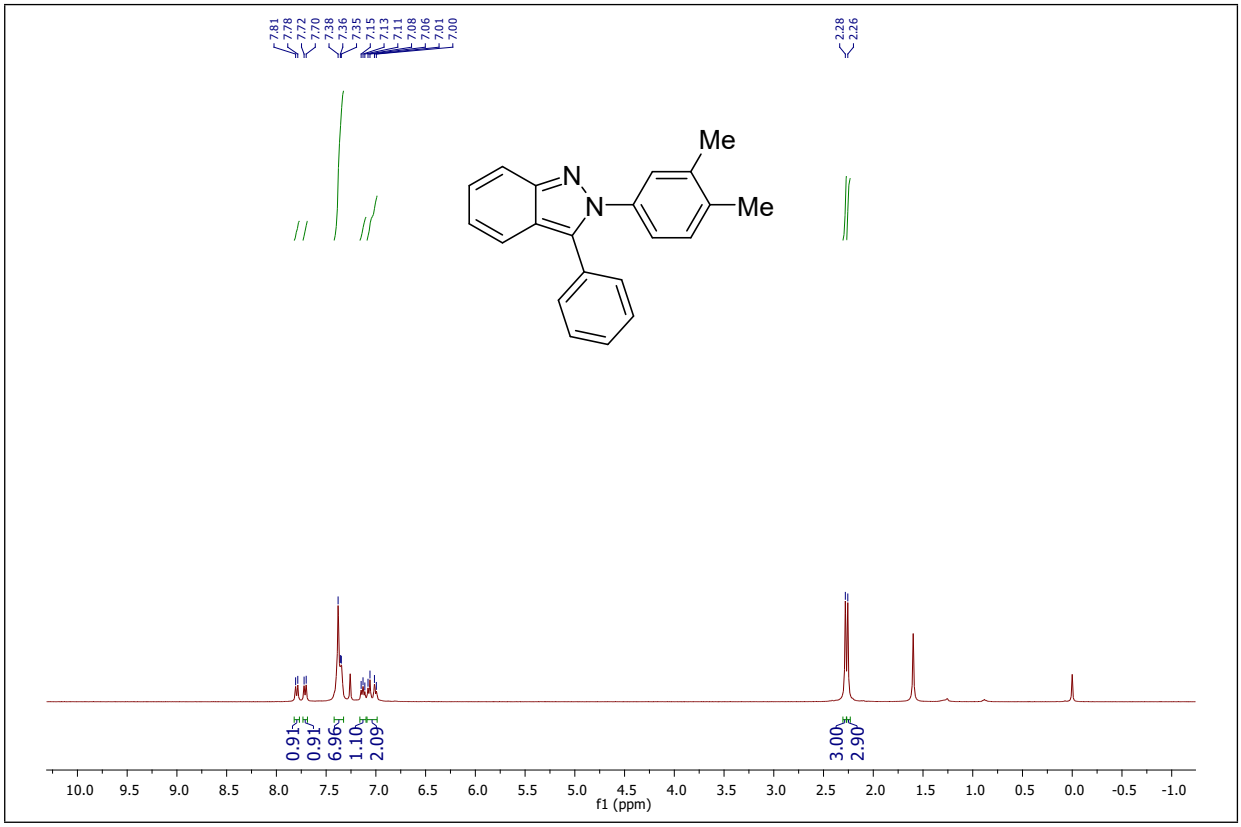
^{13}C NMR spectrum of **3ba** (101 MHz, $CDCl_3$):



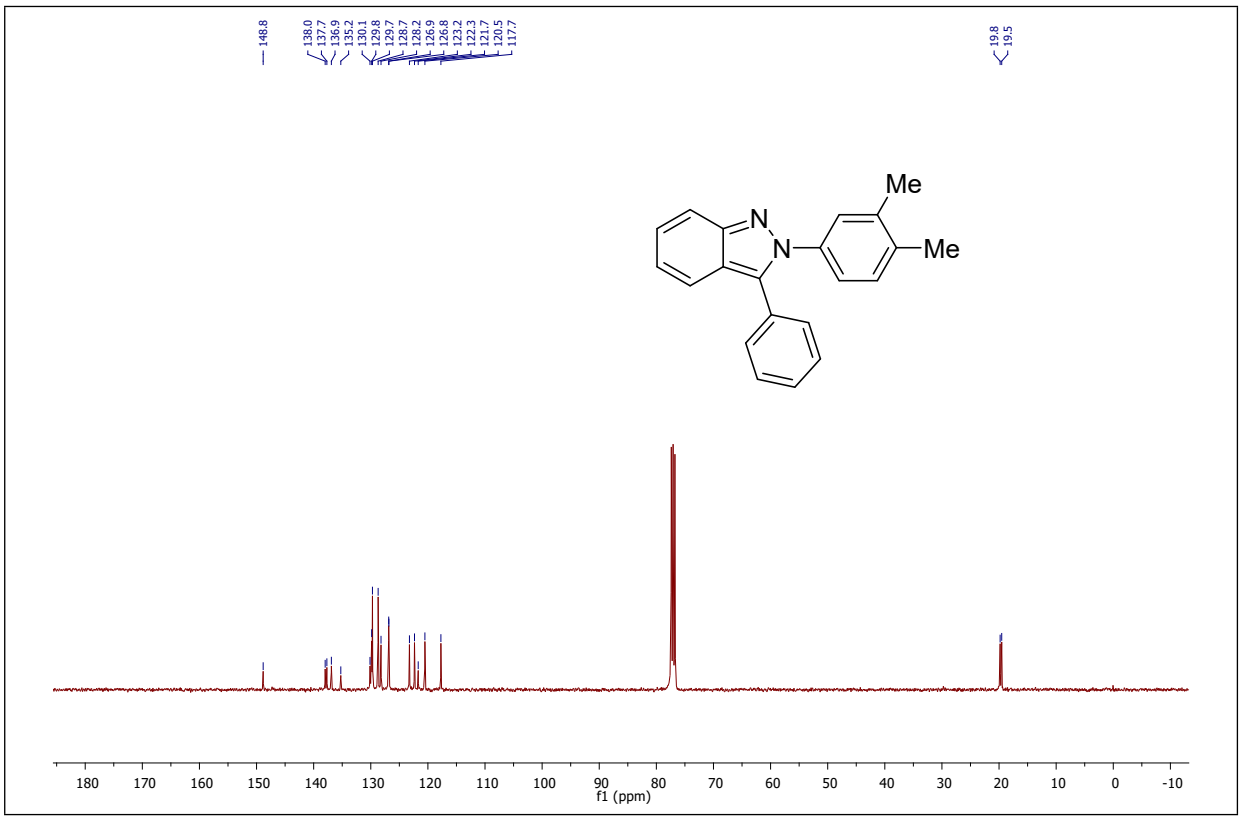
^{19}F NMR spectrum of **3ba** (377 MHz, $CDCl_3$):



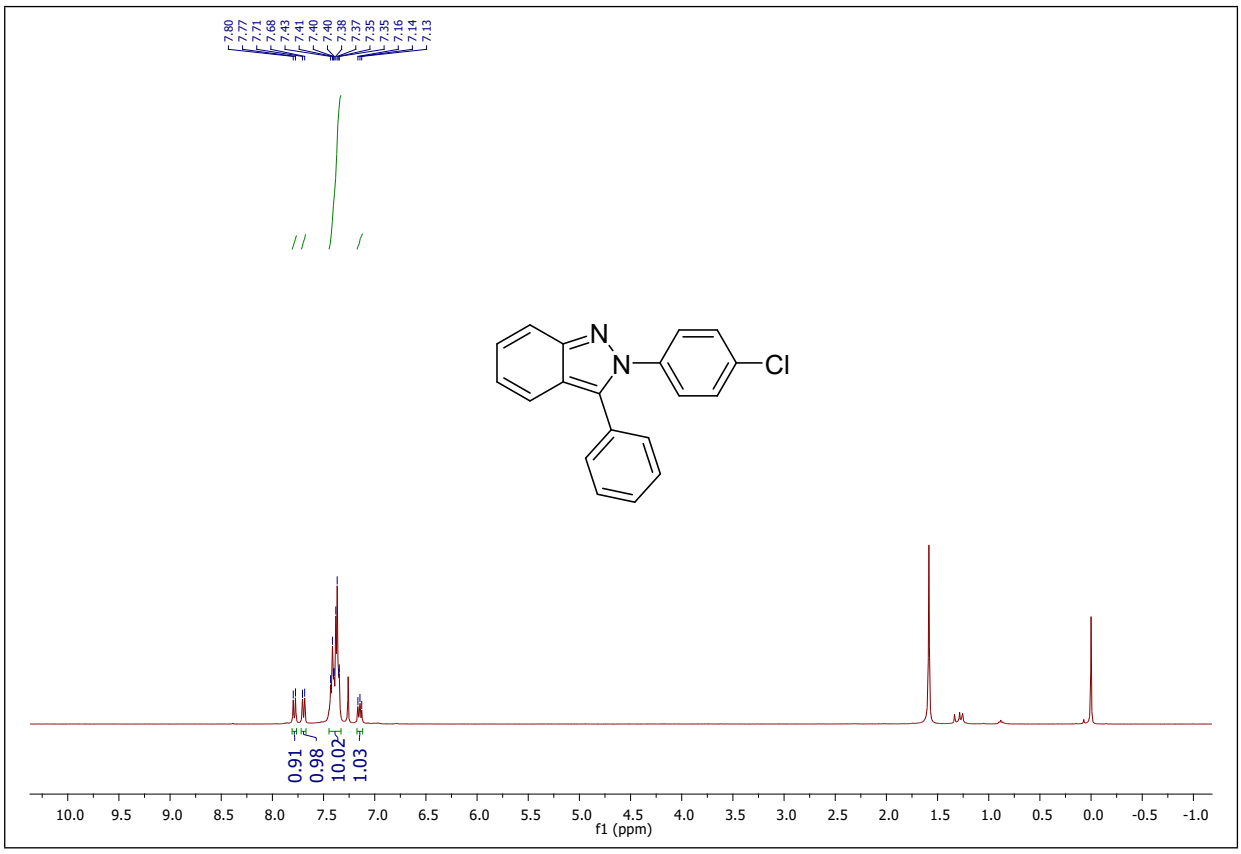
^{1}H NMR spectrum of **3ca** (400 MHz, $CDCl_3$):



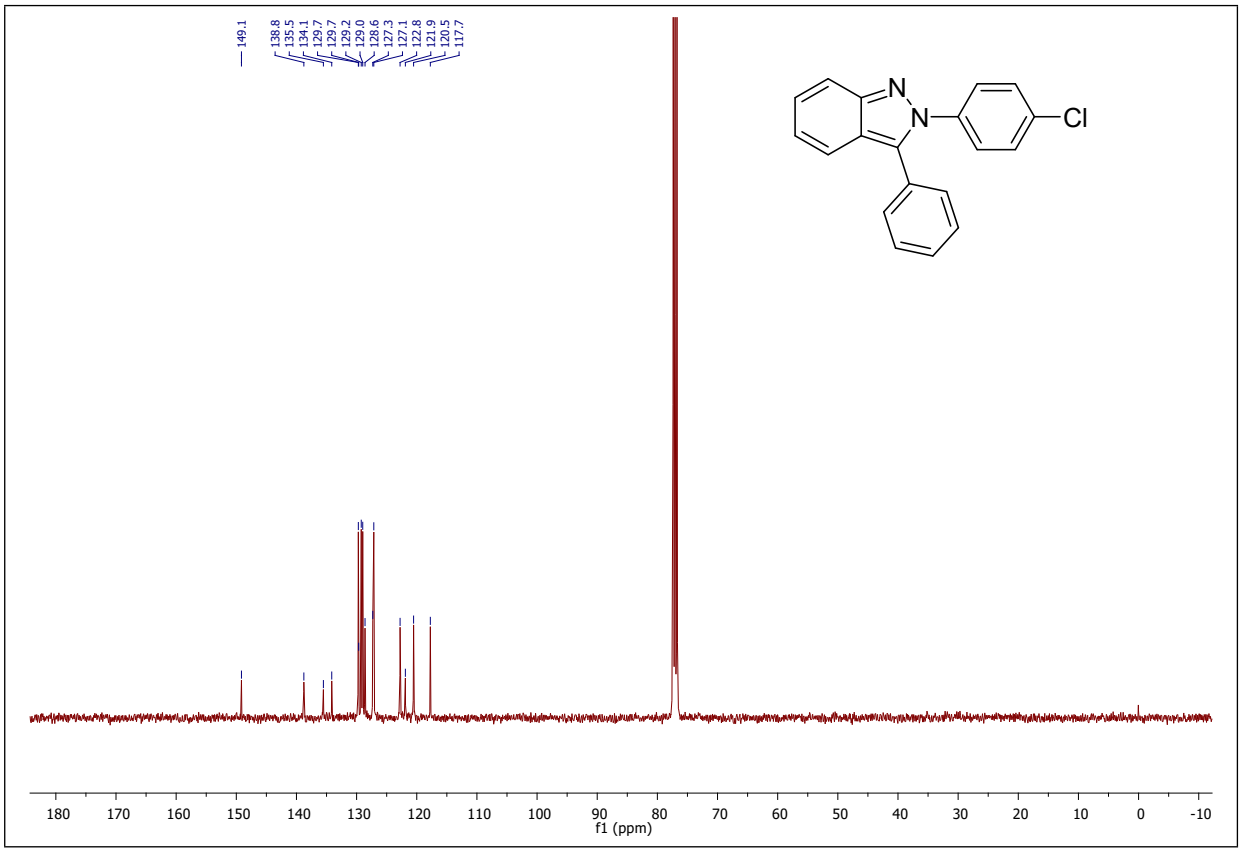
^{13}C NMR spectrum of **3ca** (101 MHz, $CDCl_3$):



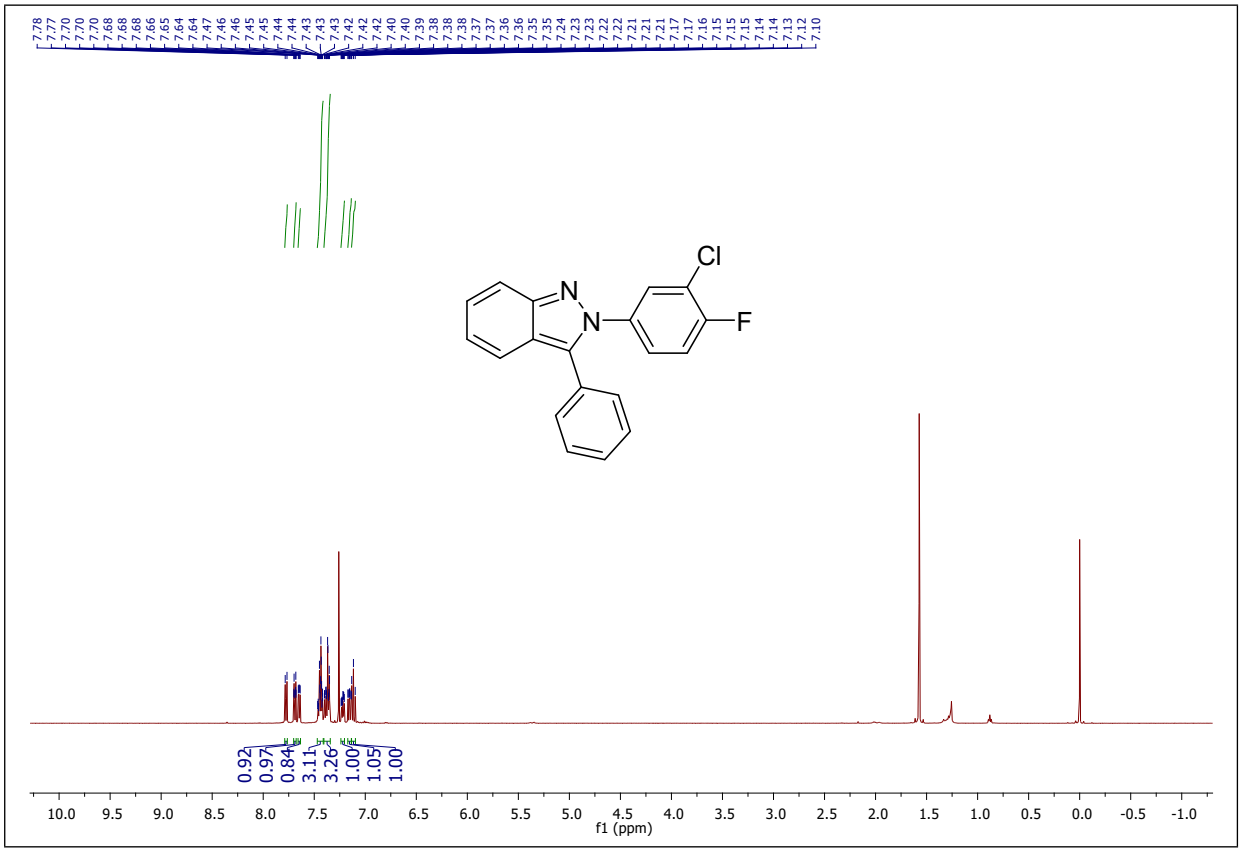
^{1}H NMR spectrum of **3da** (400 MHz, $CDCl_3$):



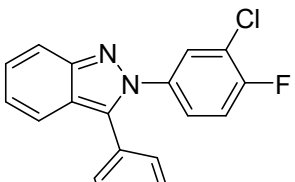
^{13}C NMR spectrum of **3da** (101 MHz, $CDCl_3$):

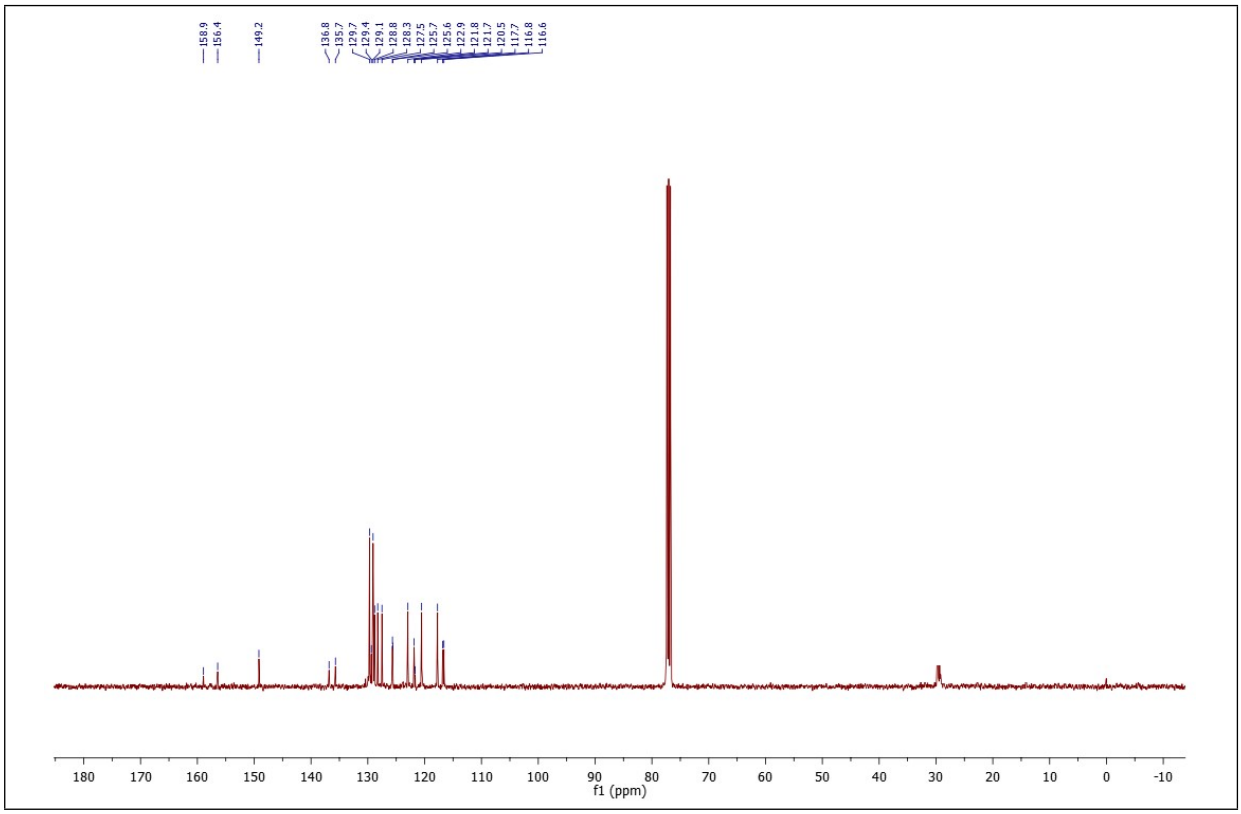


^{1}H NMR spectrum of **3ea** (500 MHz, $CDCl_3$):

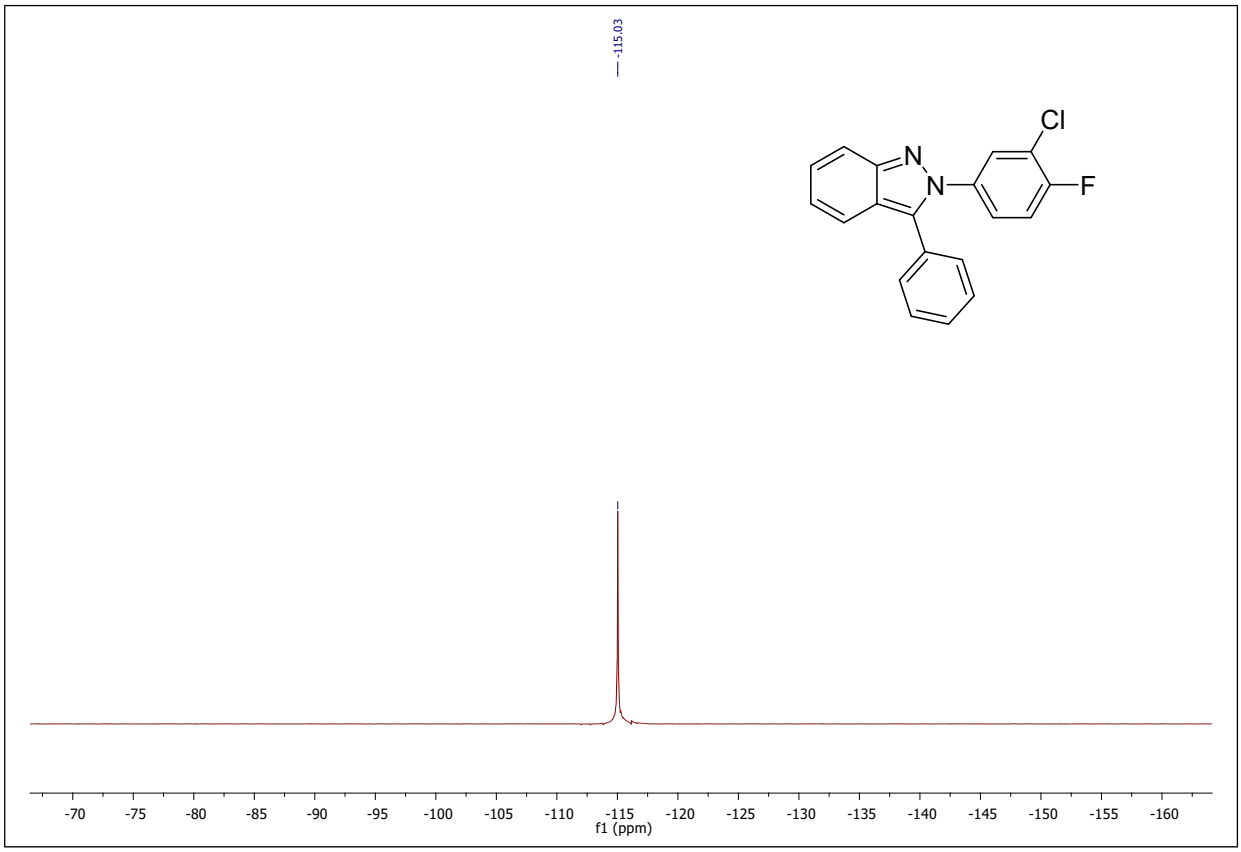


^{13}C NMR spectrum of **3ea** (101 MHz, $CDCl_3$):

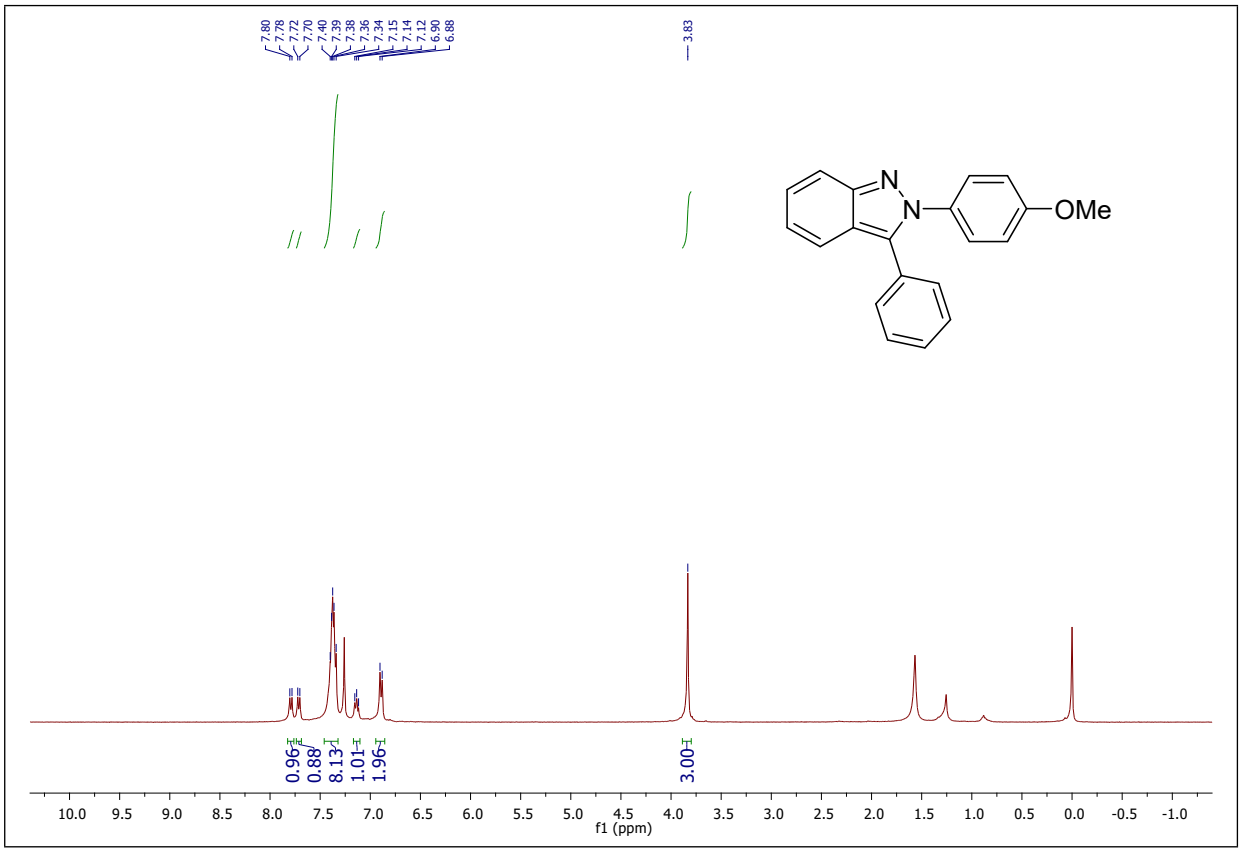




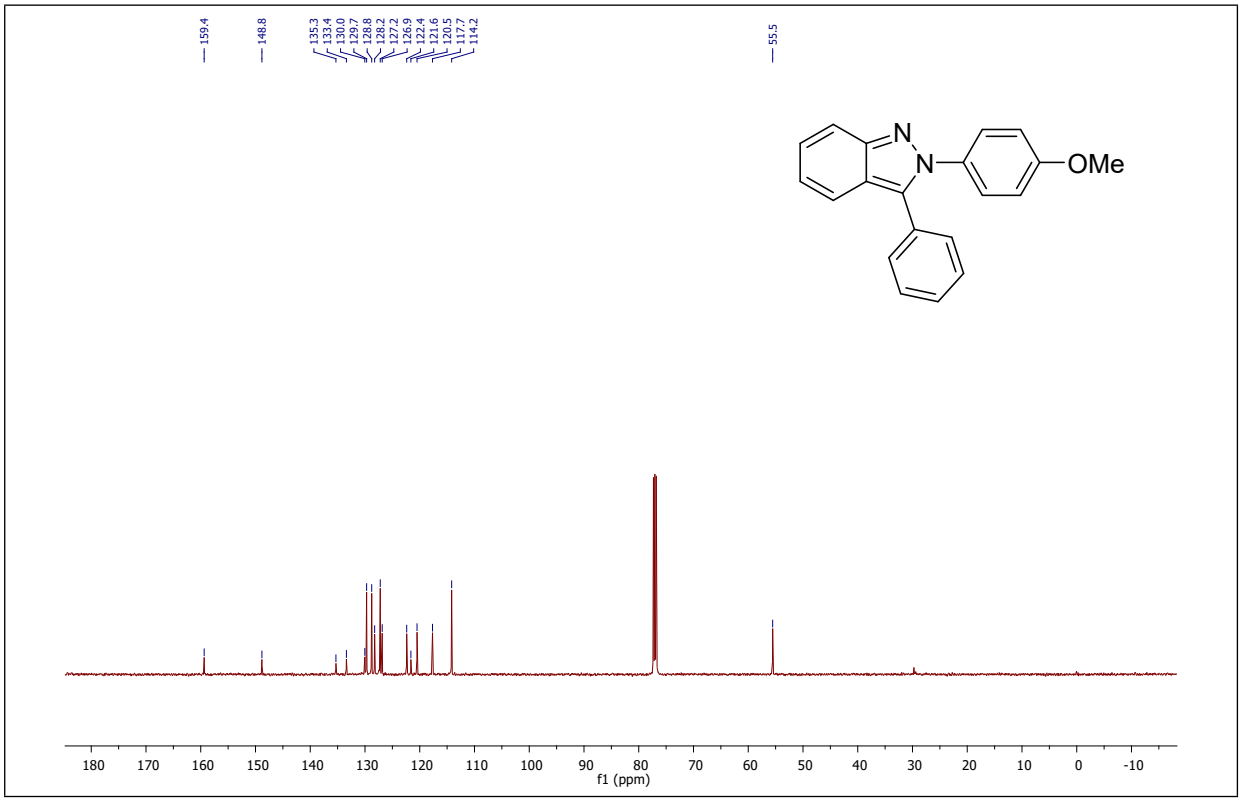
^{19}F NMR spectrum of **3bb** (377 MHz, $CDCl_3$):



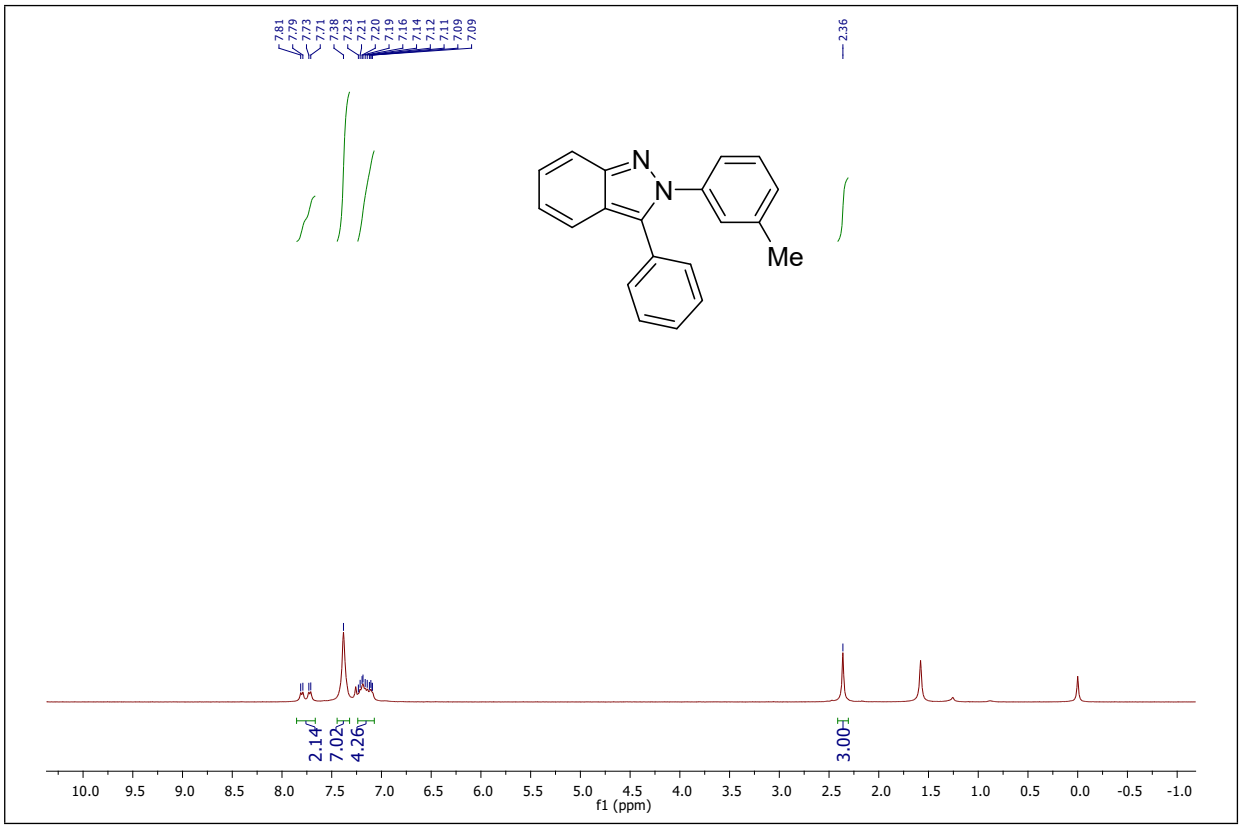
^{1}H NMR spectrum of **3fa** (400 MHz, $CDCl_3$):



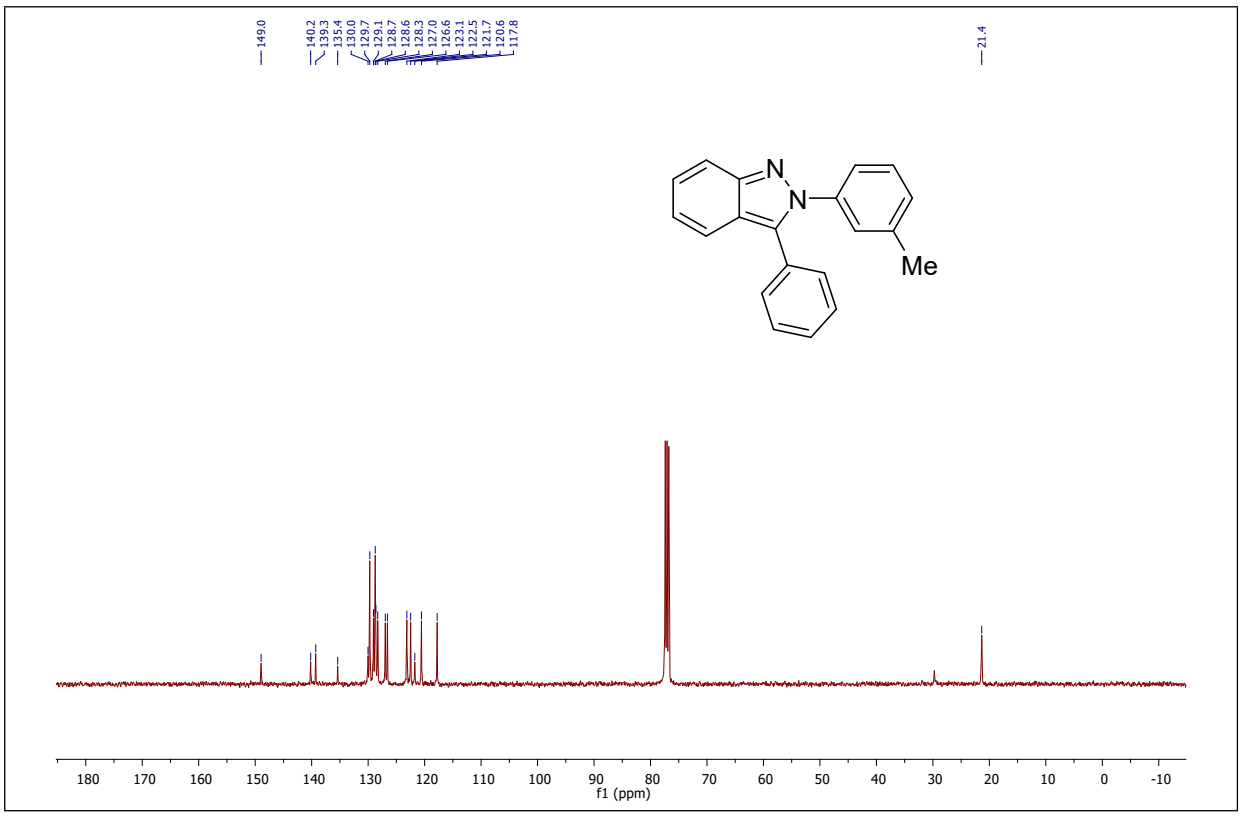
^{13}C NMR spectrum of **3fa** (126 MHz, $CDCl_3$):



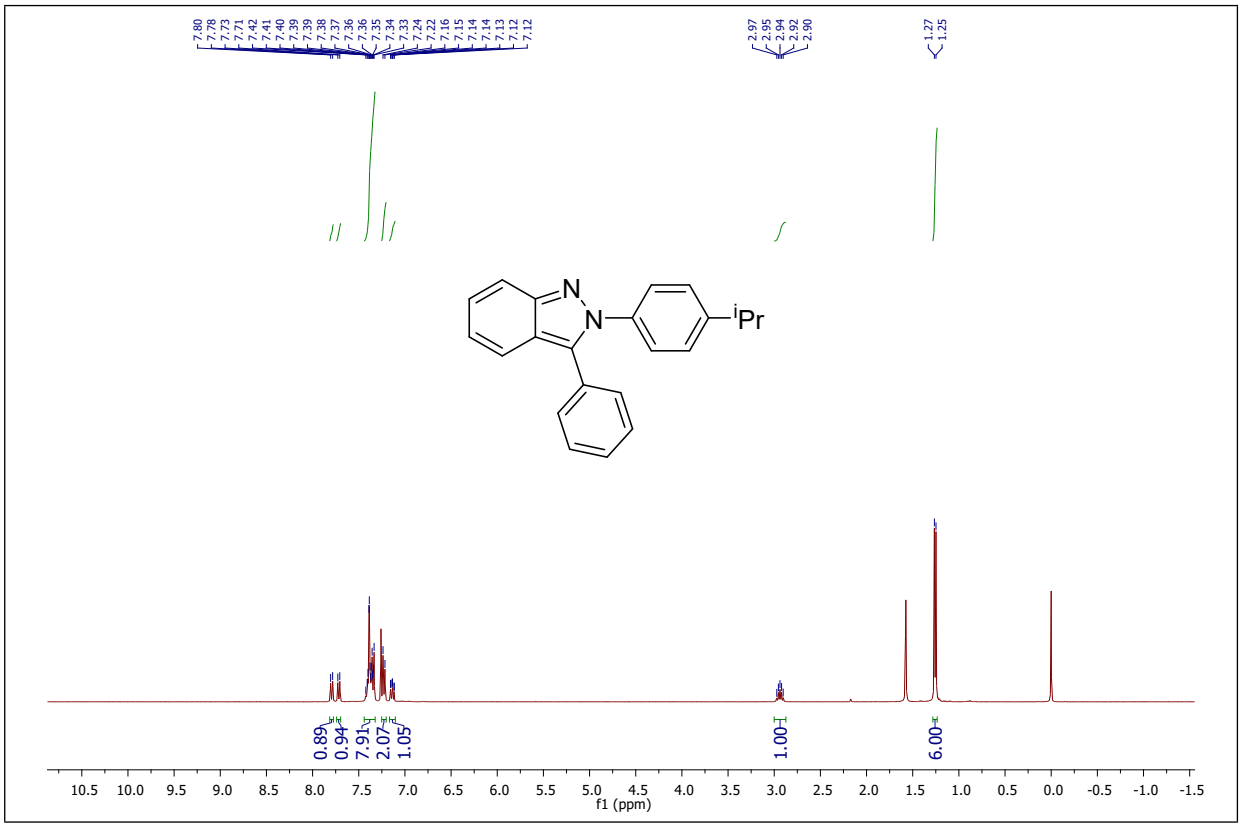
^{1}H NMR spectrum of **3ga** (400 MHz, $CDCl_3$):



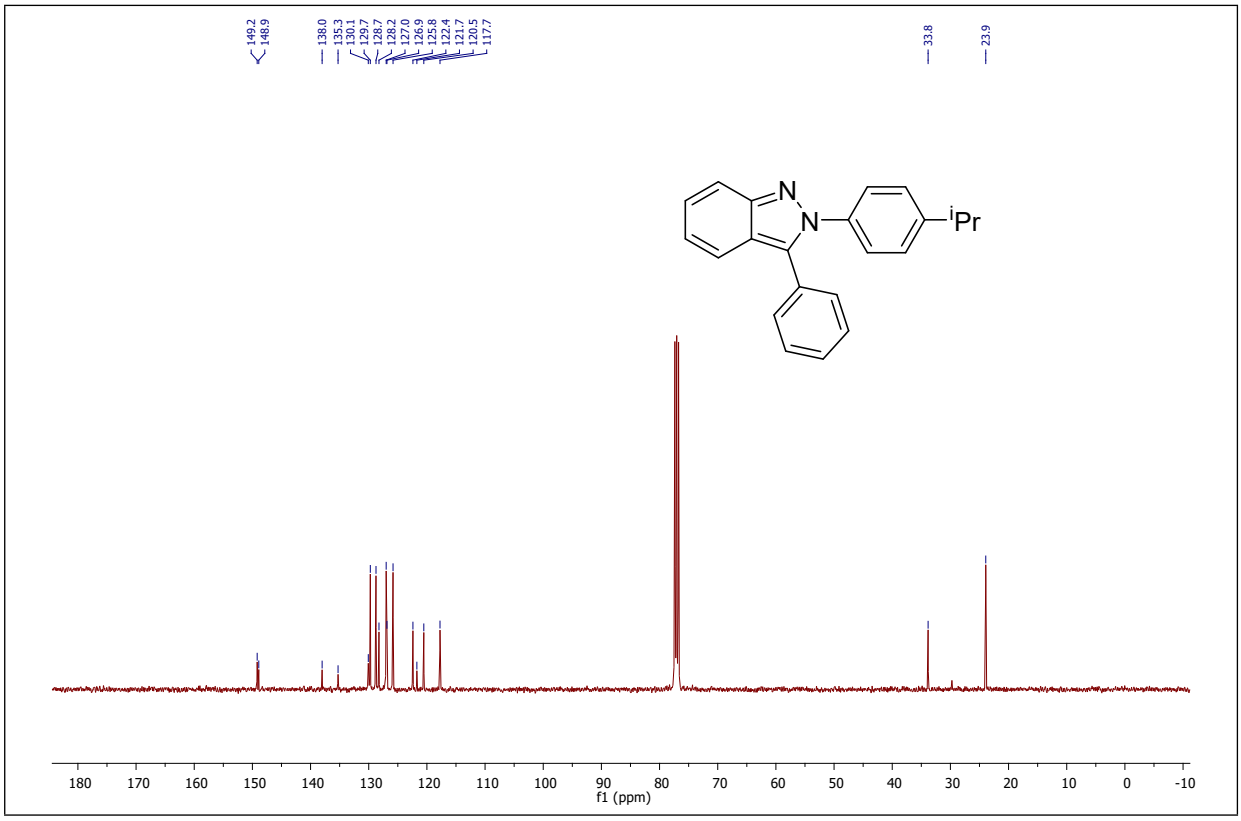
^{13}C NMR spectrum of **3ga** (101 MHz, $CDCl_3$):



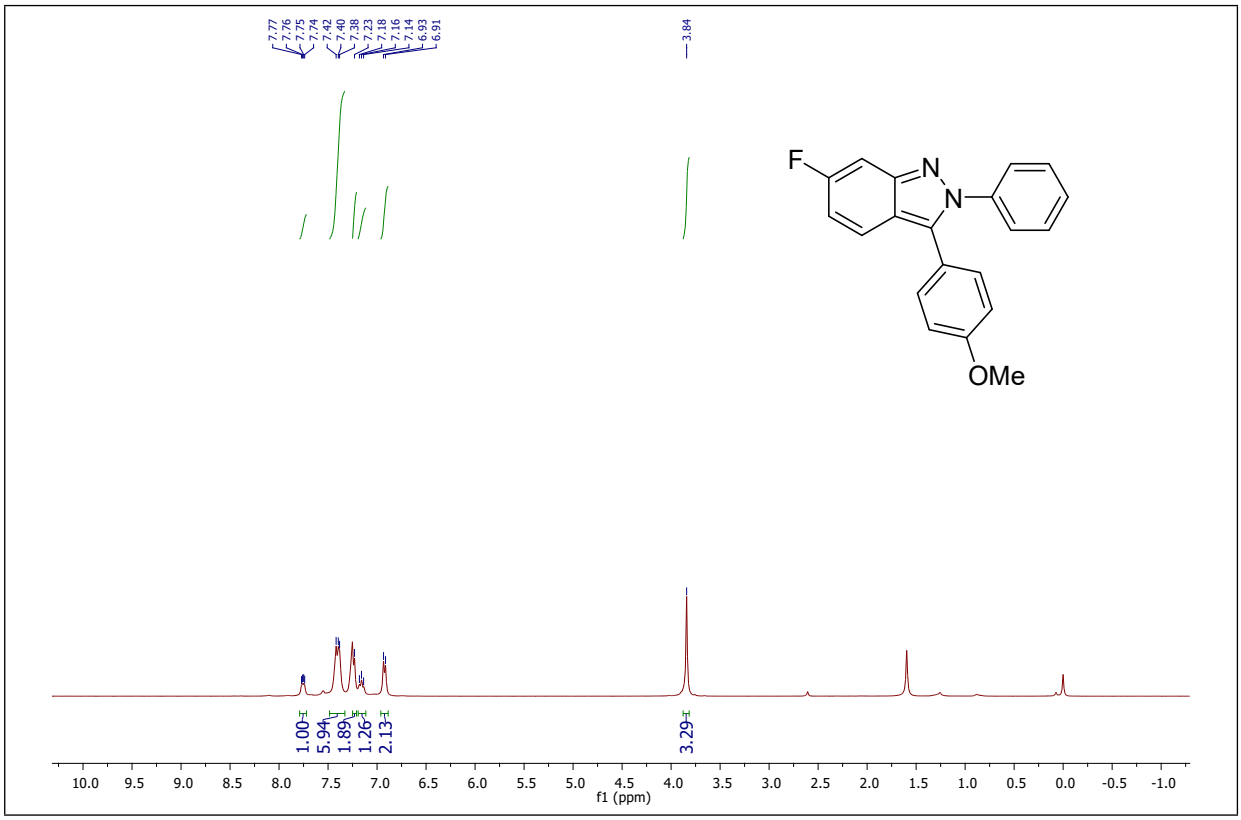
^{1}H NMR spectrum of **3ha** (400 MHz, $CDCl_3$):



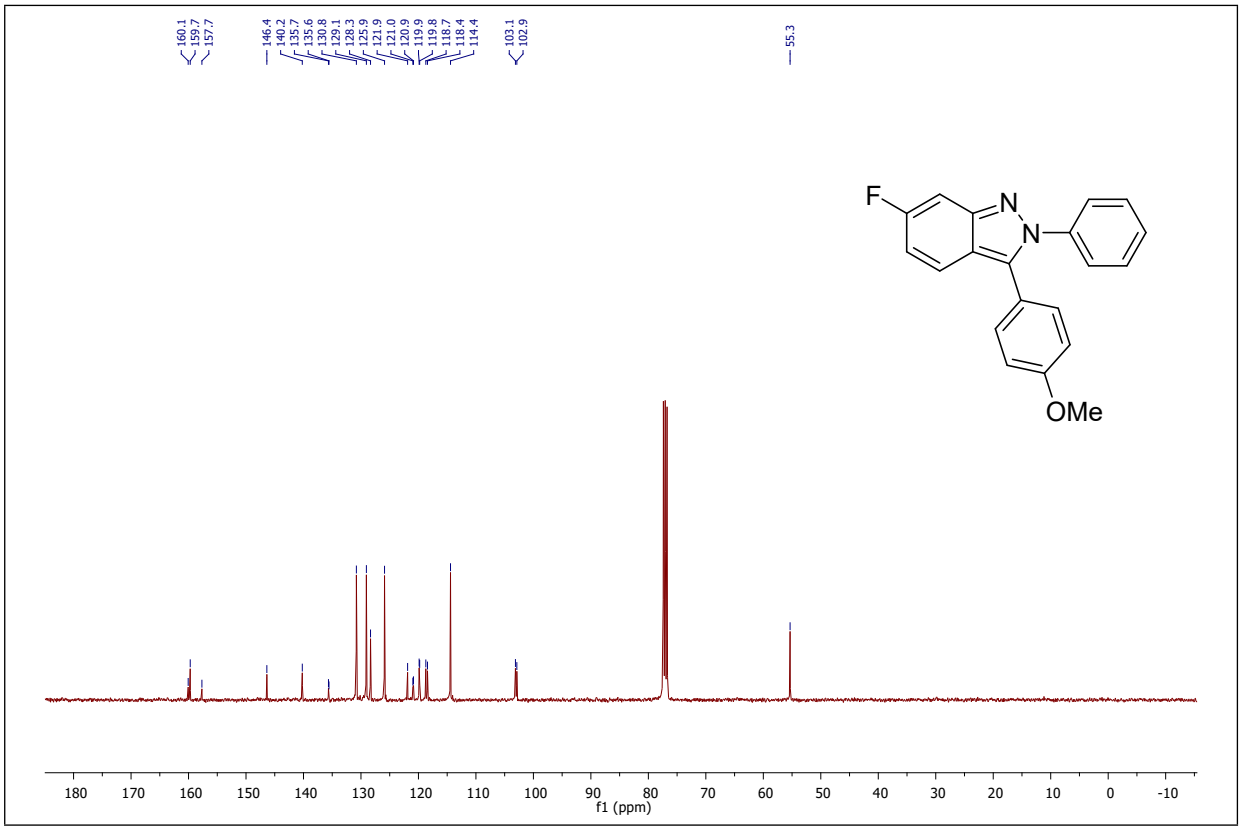
^{13}C NMR spectrum of **3ha** (101 MHz, $CDCl_3$):



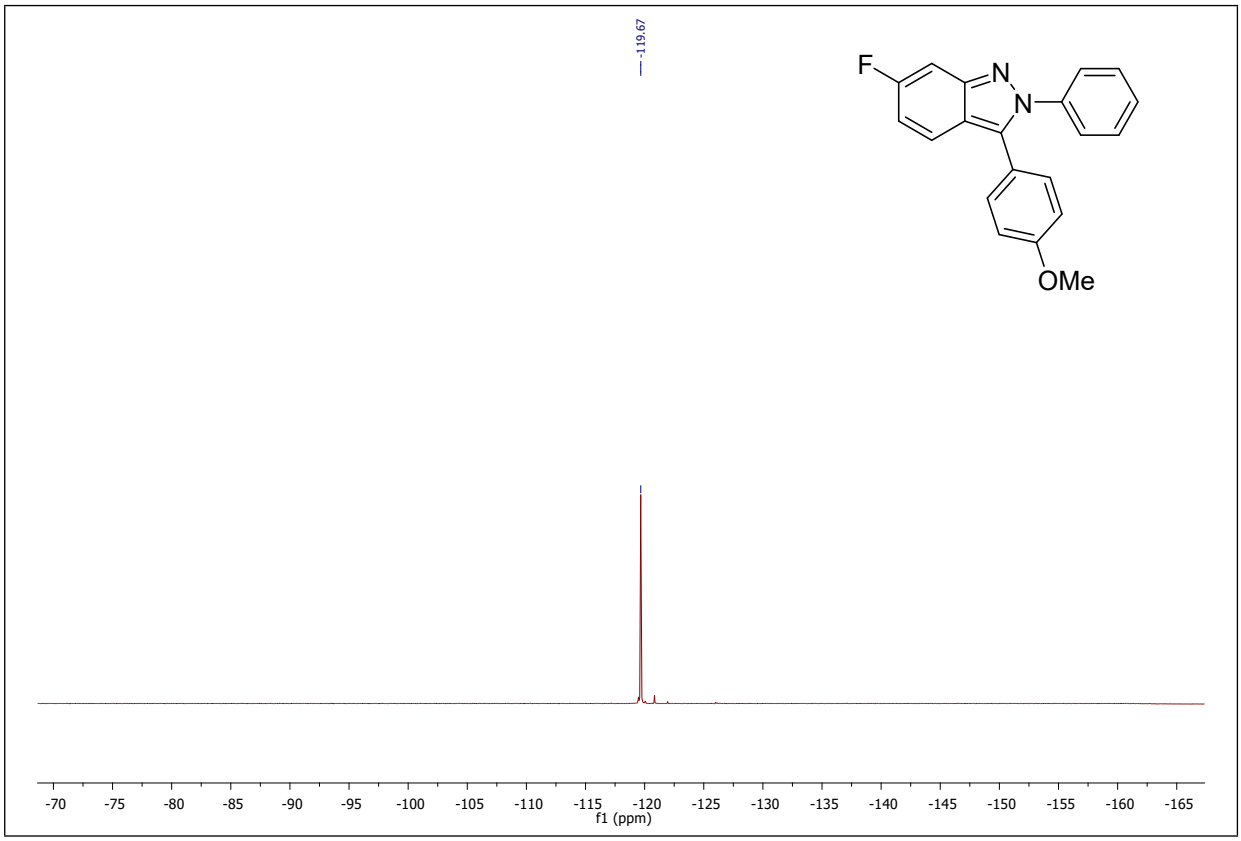
^{1}H NMR spectrum of **3bb** (400 MHz, $CDCl_3$):



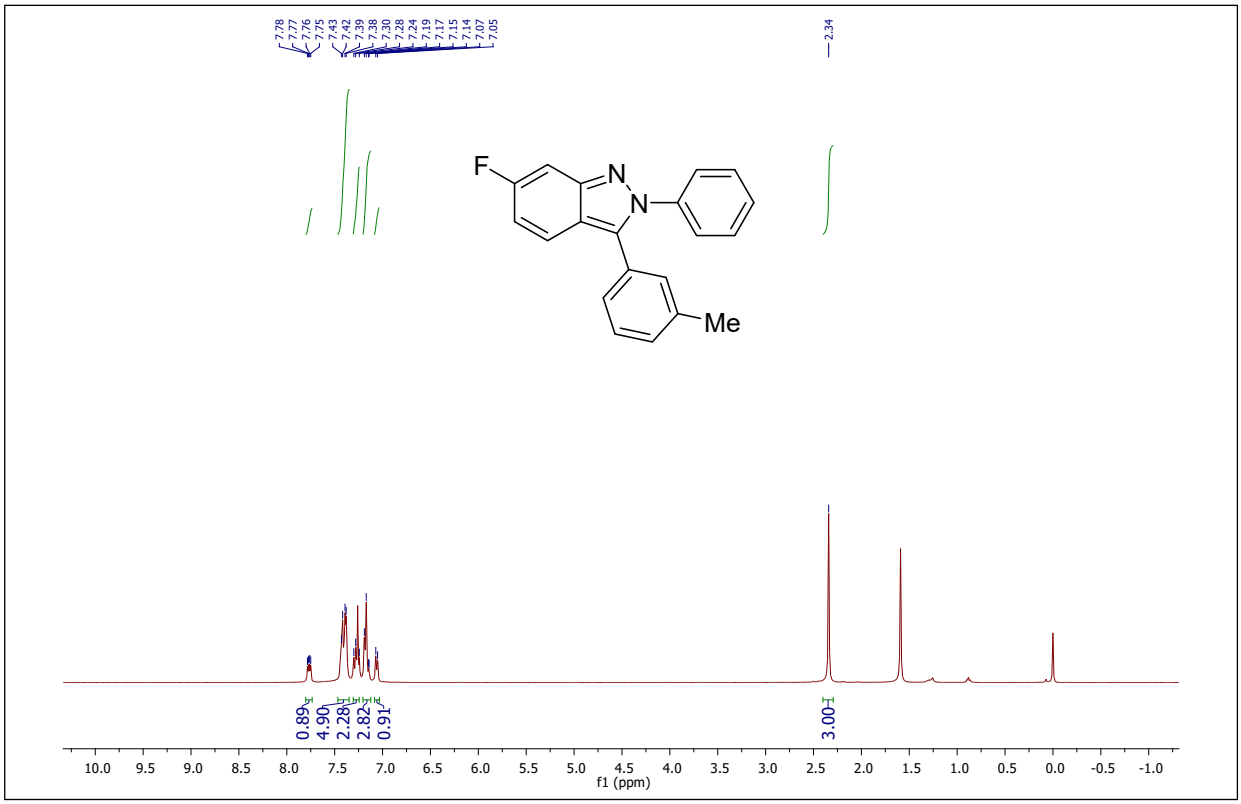
^{13}C NMR spectrum of **3bb** (101 MHz, $CDCl_3$):



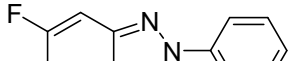
^{19}F NMR spectrum of **3bb** (376 MHz, $CDCl_3$):

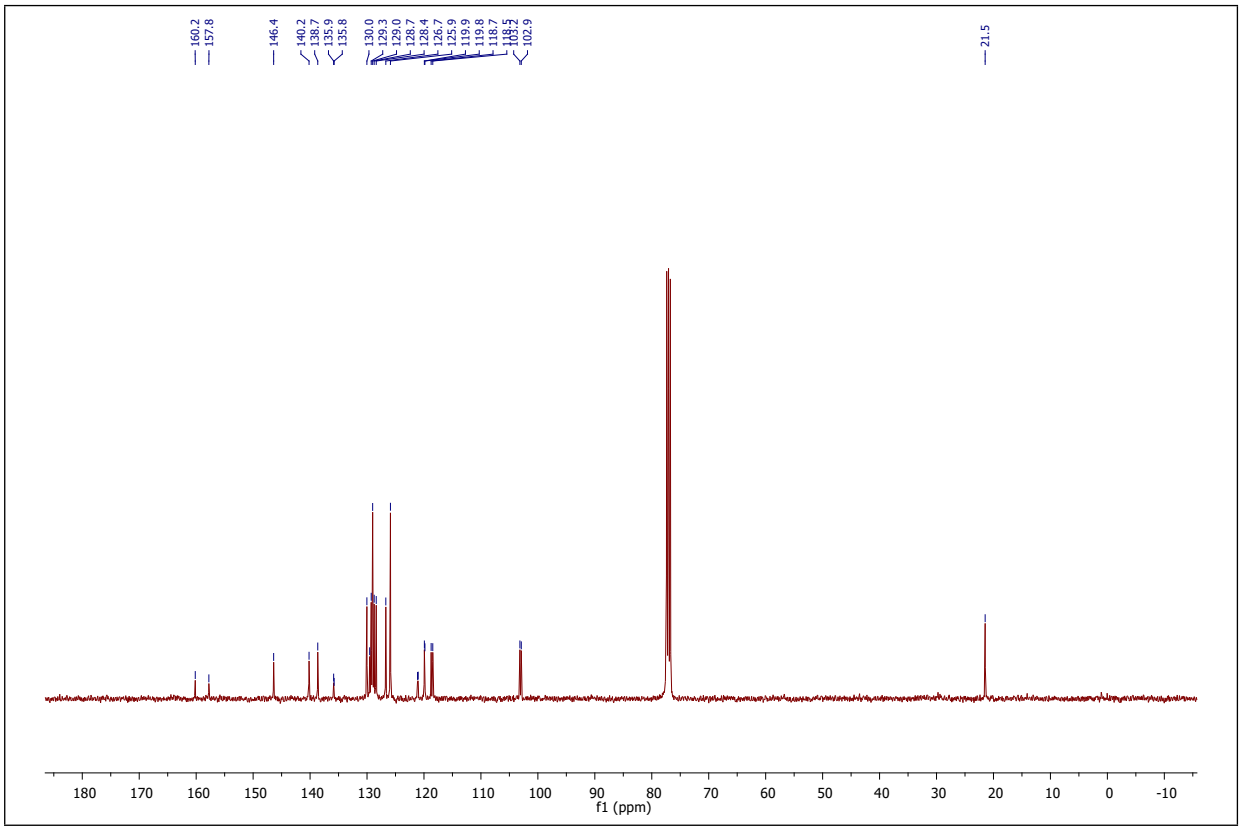


^{1}H NMR spectrum of **3bc** (400 MHz, $CDCl_3$):

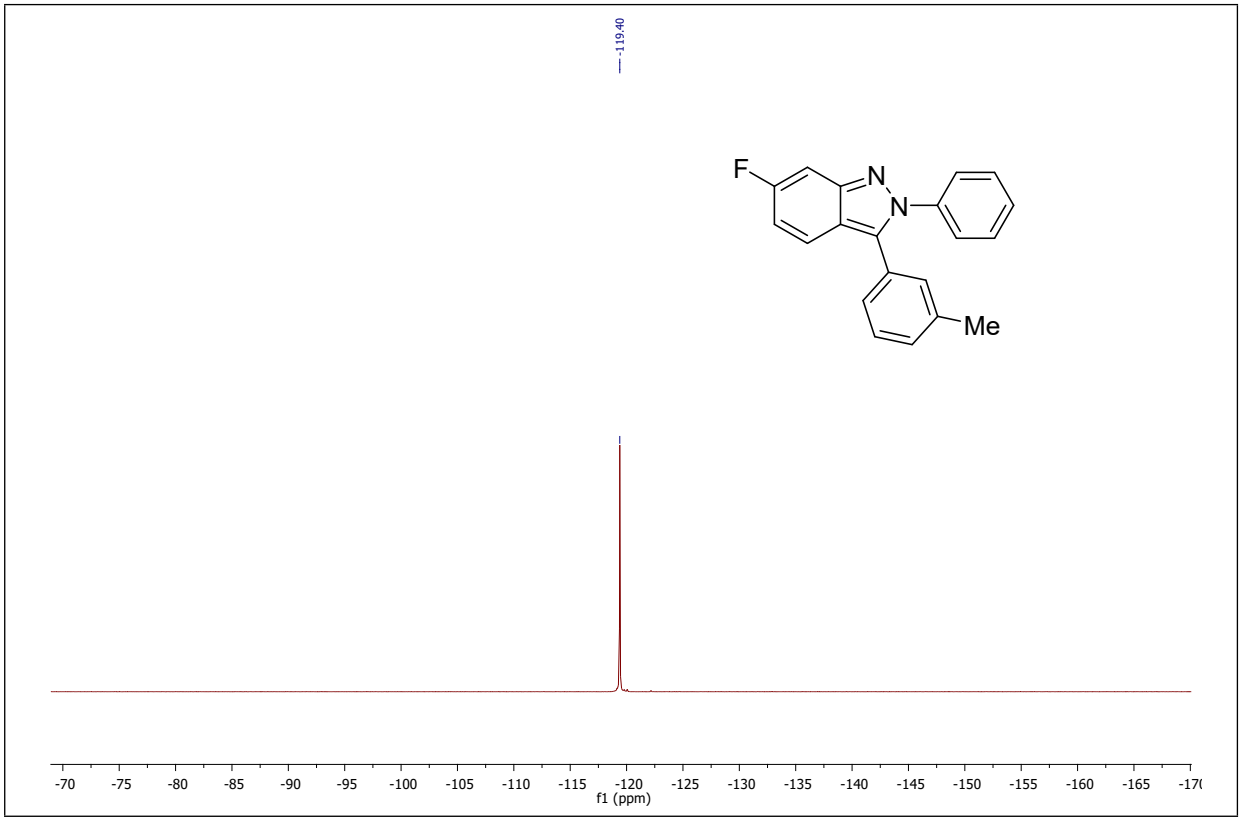


^{13}C NMR spectrum of **3bc** (101 MHz, $CDCl_3$):

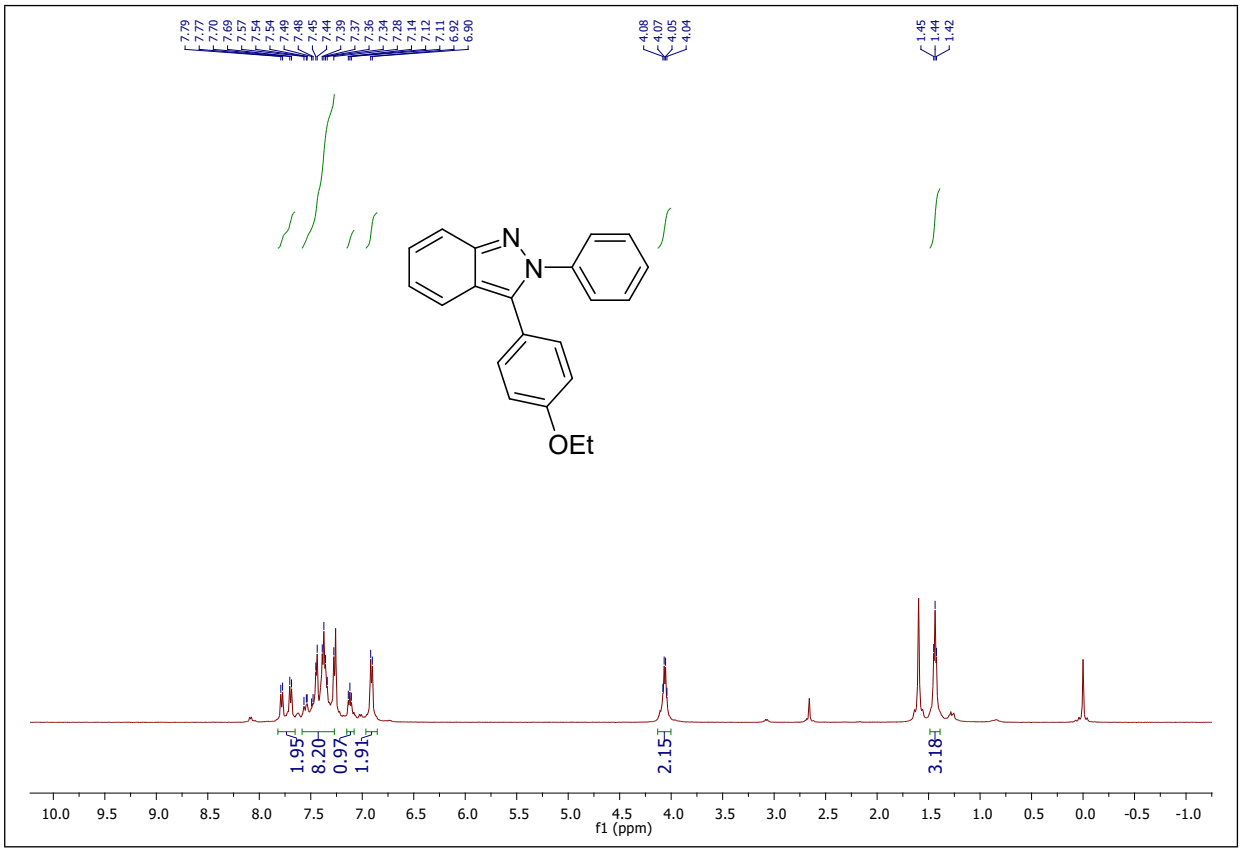




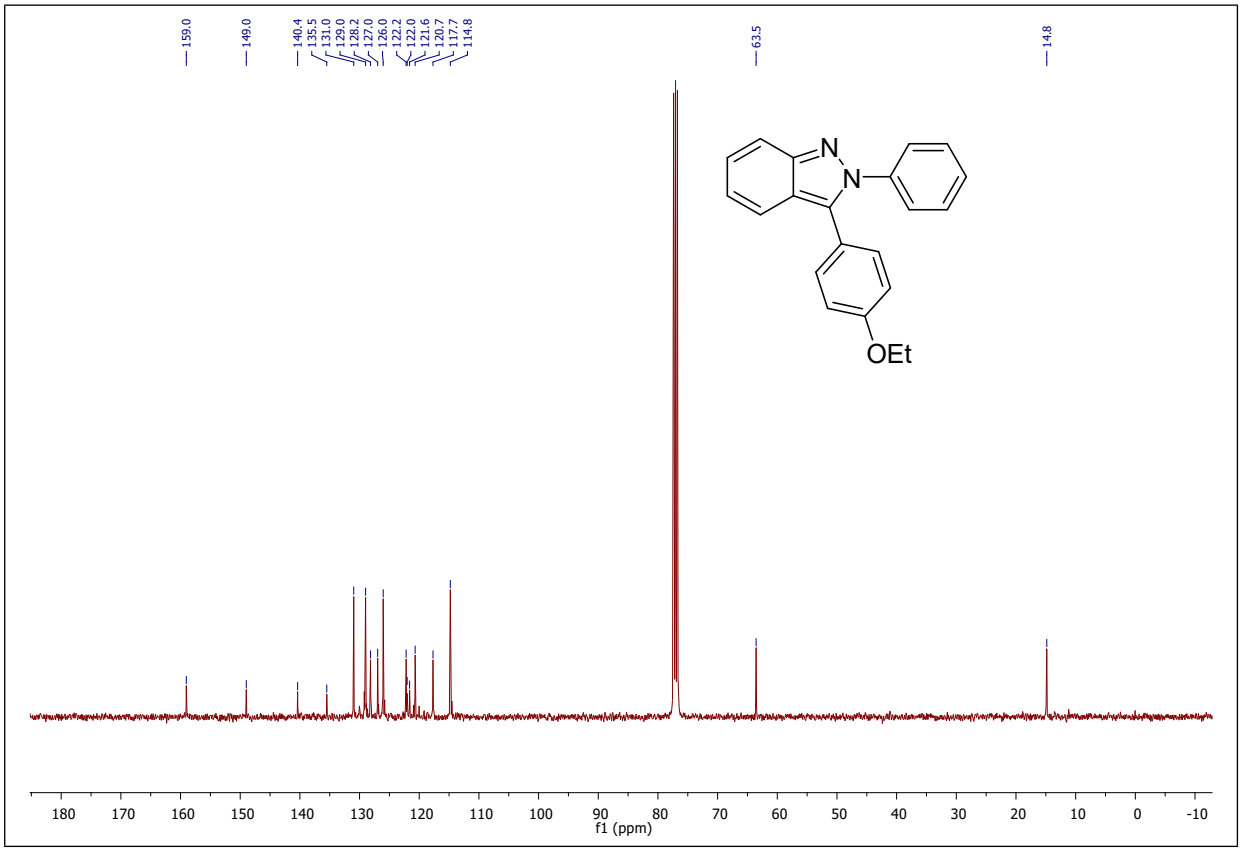
^{19}F NMR spectrum of **3bc** (377 MHz, $CDCl_3$):



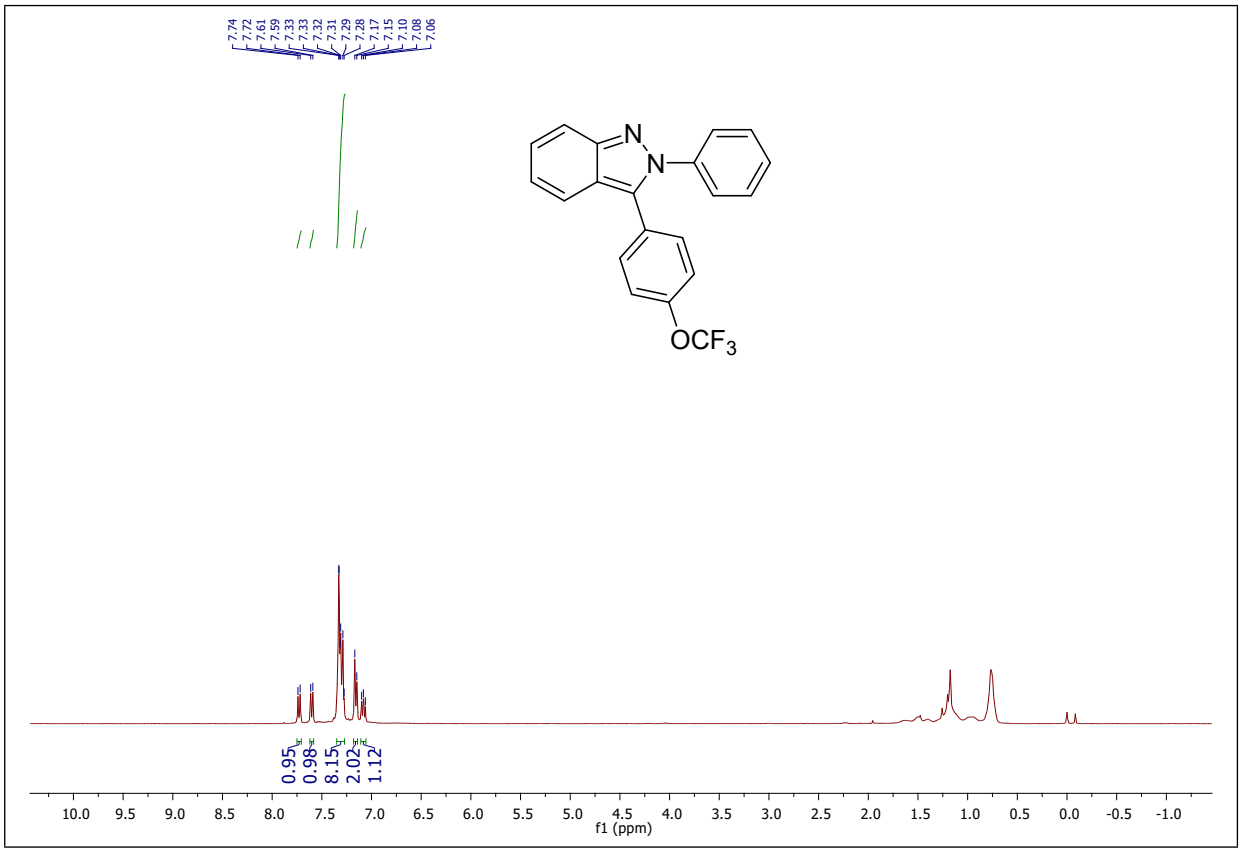
^{1}H NMR spectrum of **3ad** (500 MHz, $CDCl_3$):



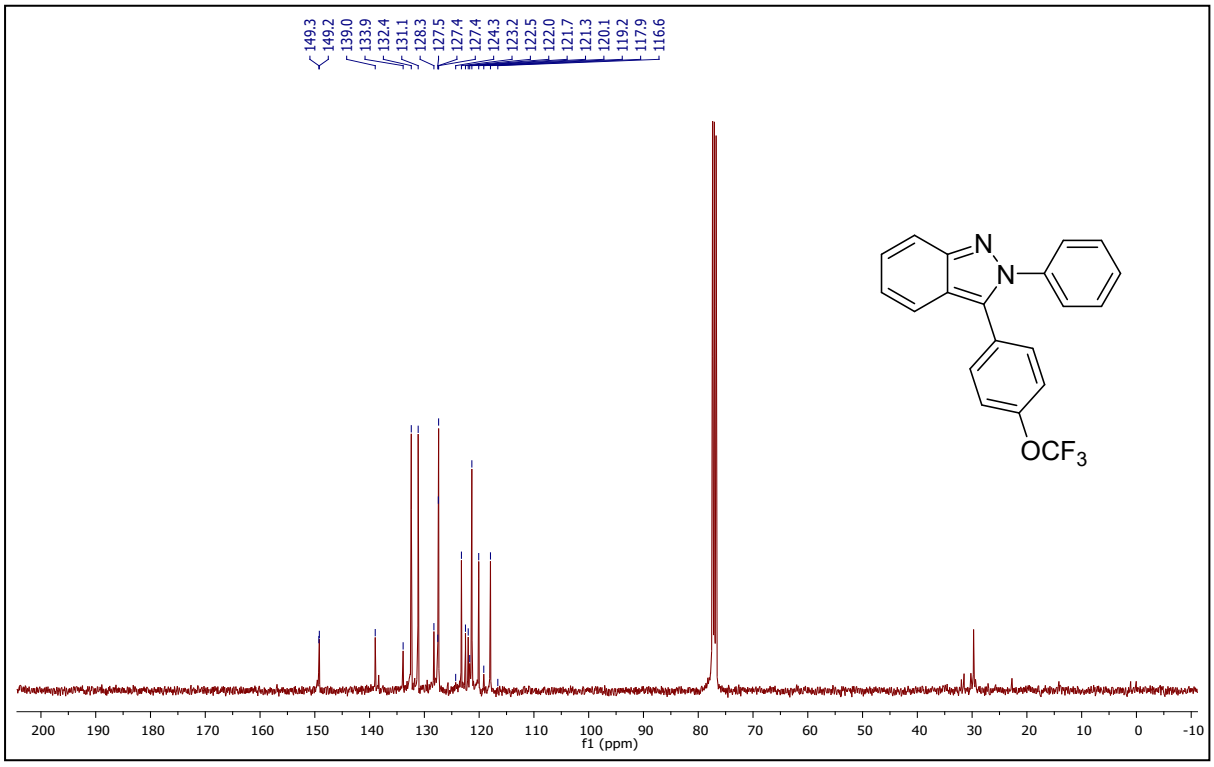
^{13}C NMR spectrum of **3ad** (101 MHz, $CDCl_3$):



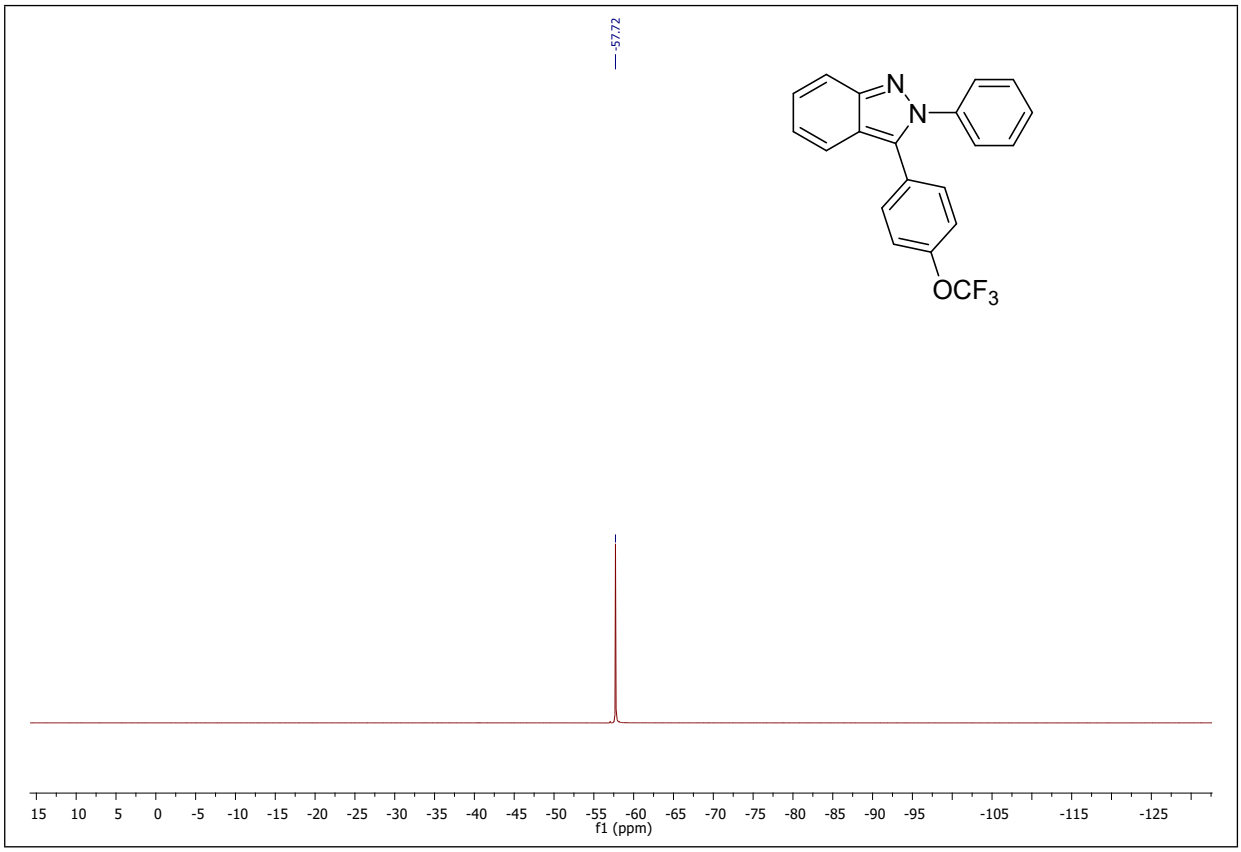
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$):



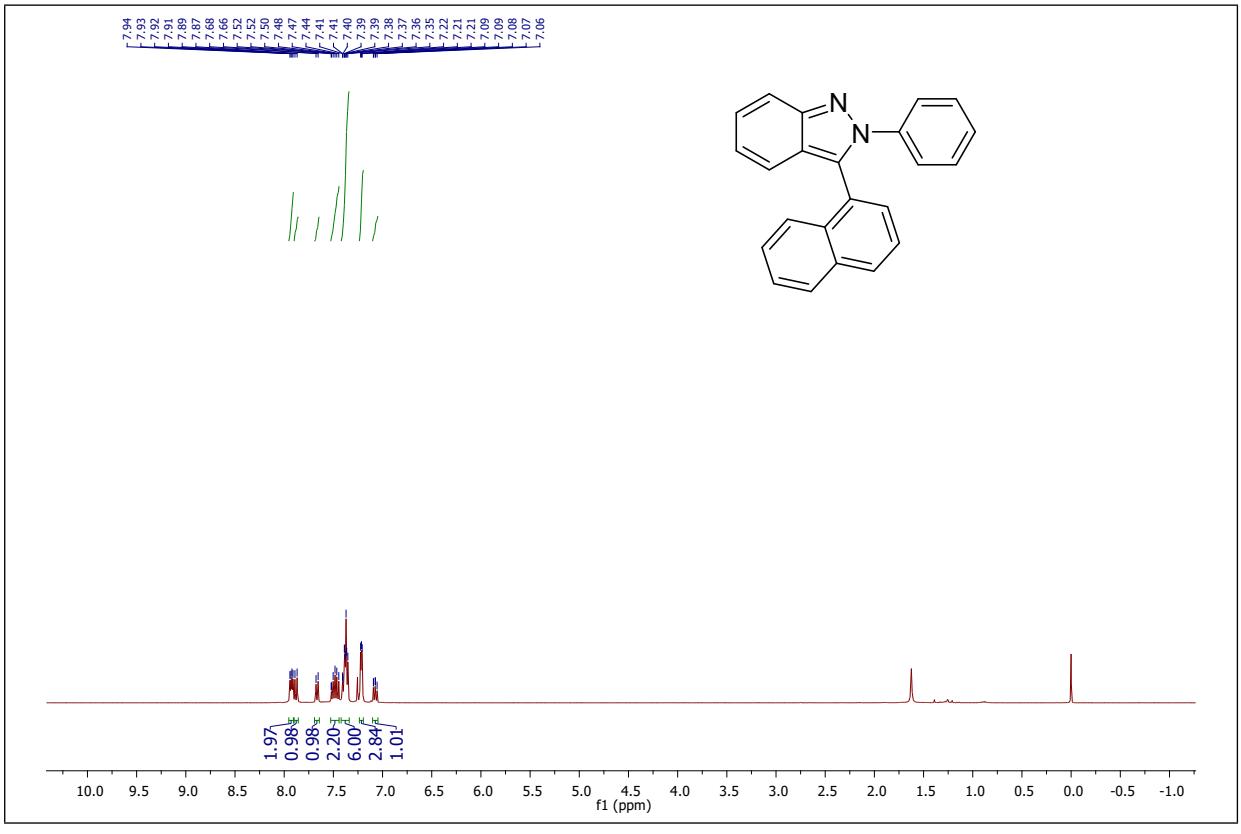
^{13}C NMR spectrum of **3ae** (101 MHz, $CDCl_3$):



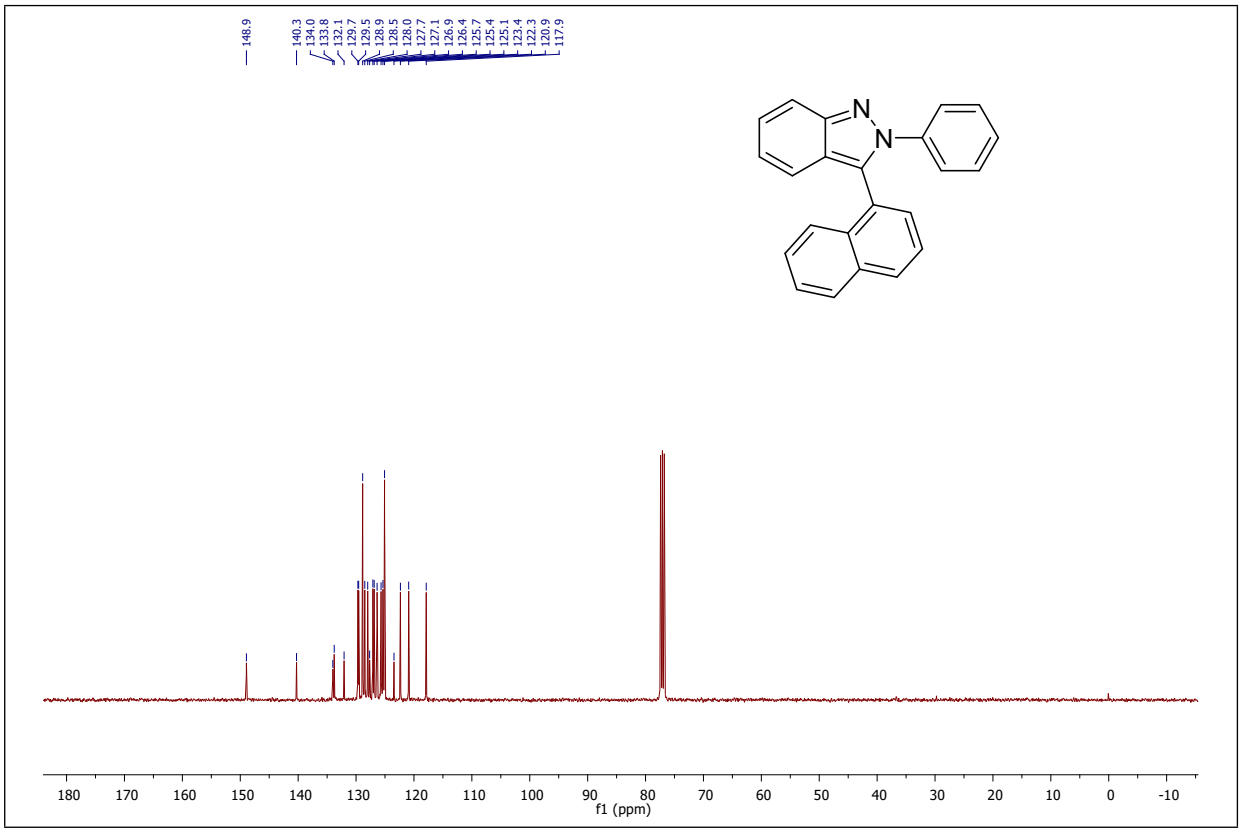
^{19}F NMR spectrum of **3ae** (377 MHz, $CDCl_3$):



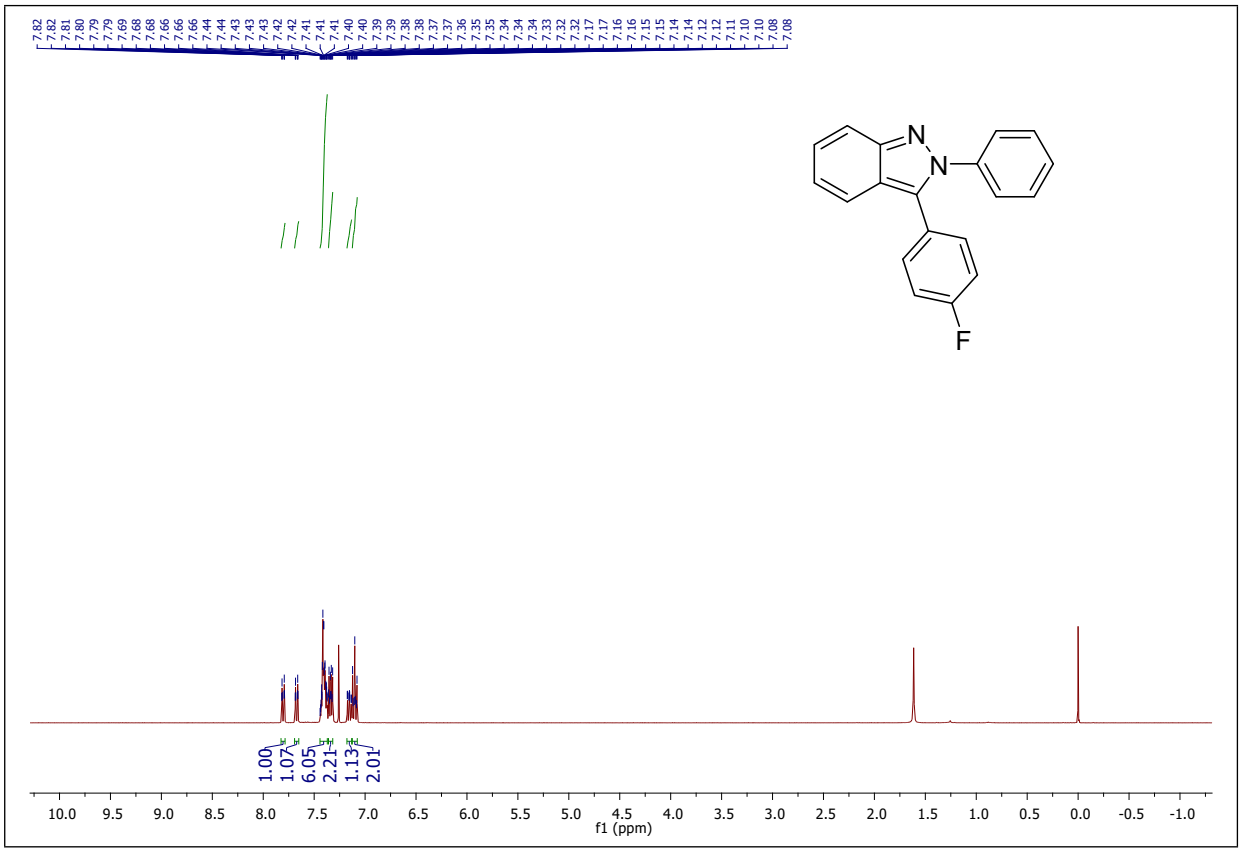
^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$):



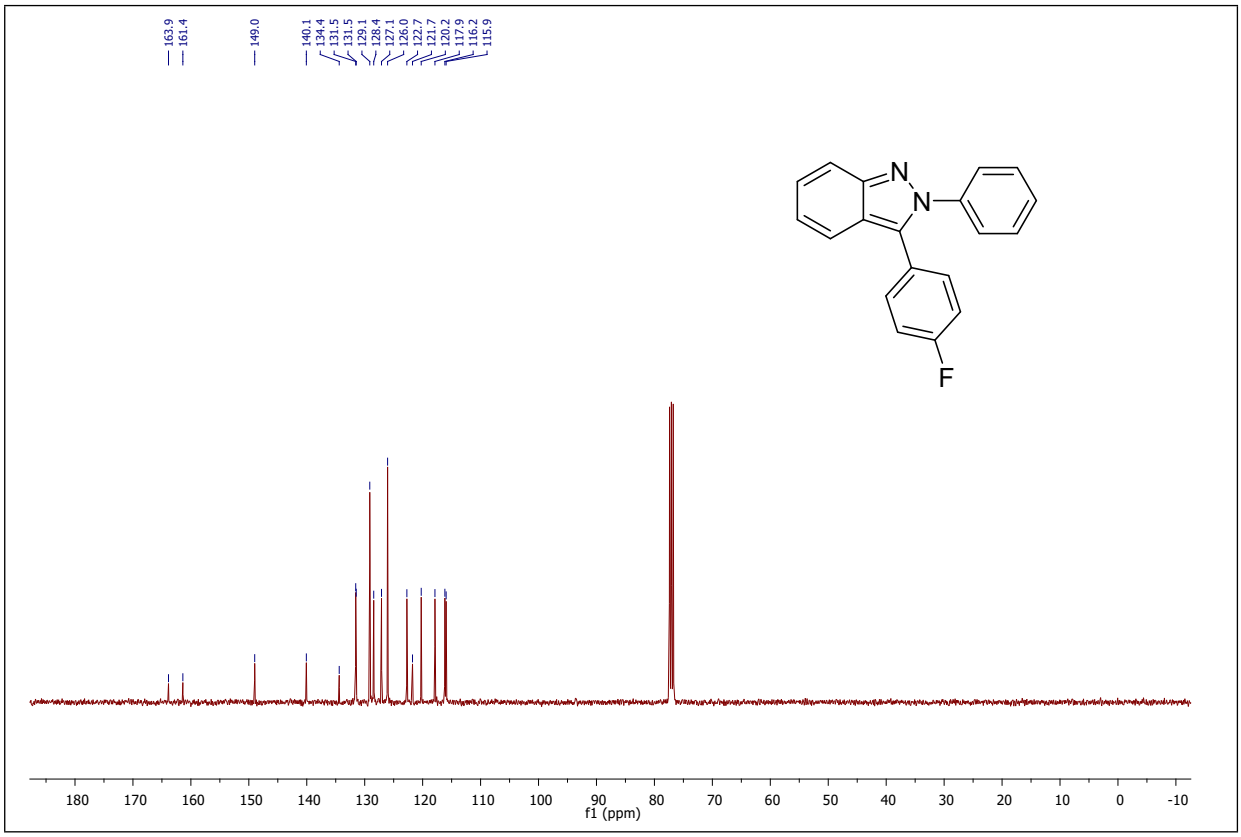
^{13}C NMR spectrum of **3af** (101 MHz, $CDCl_3$):



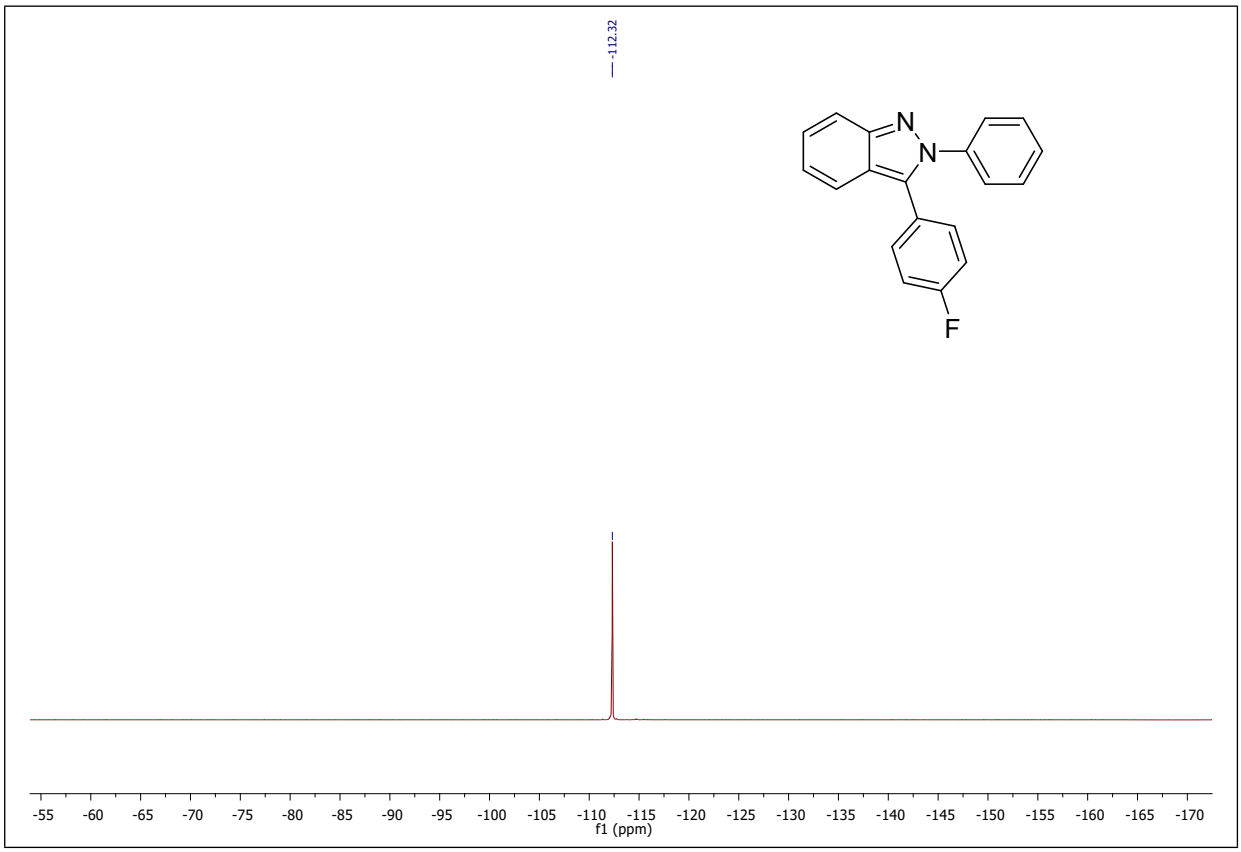
^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$):



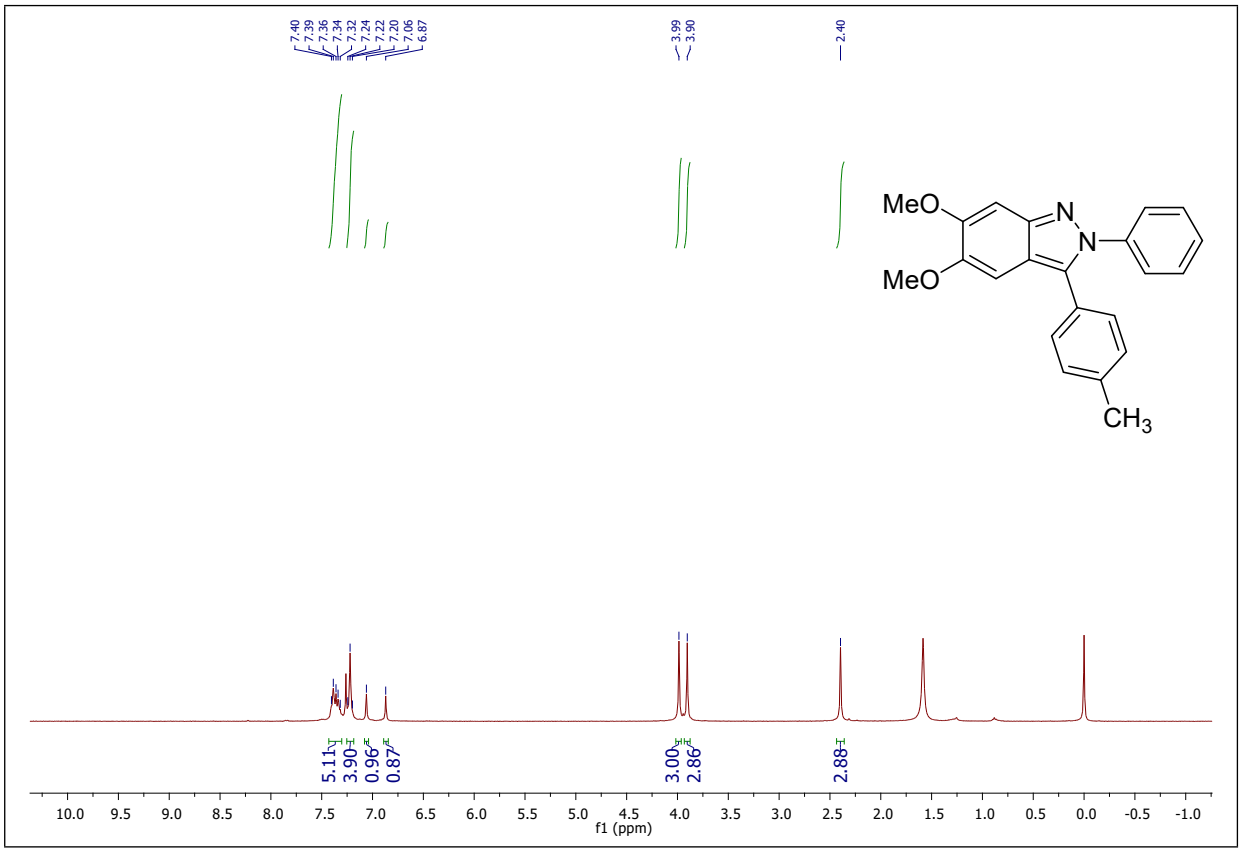
^{13}C NMR spectrum of **3ag** (101 MHz, $CDCl_3$):



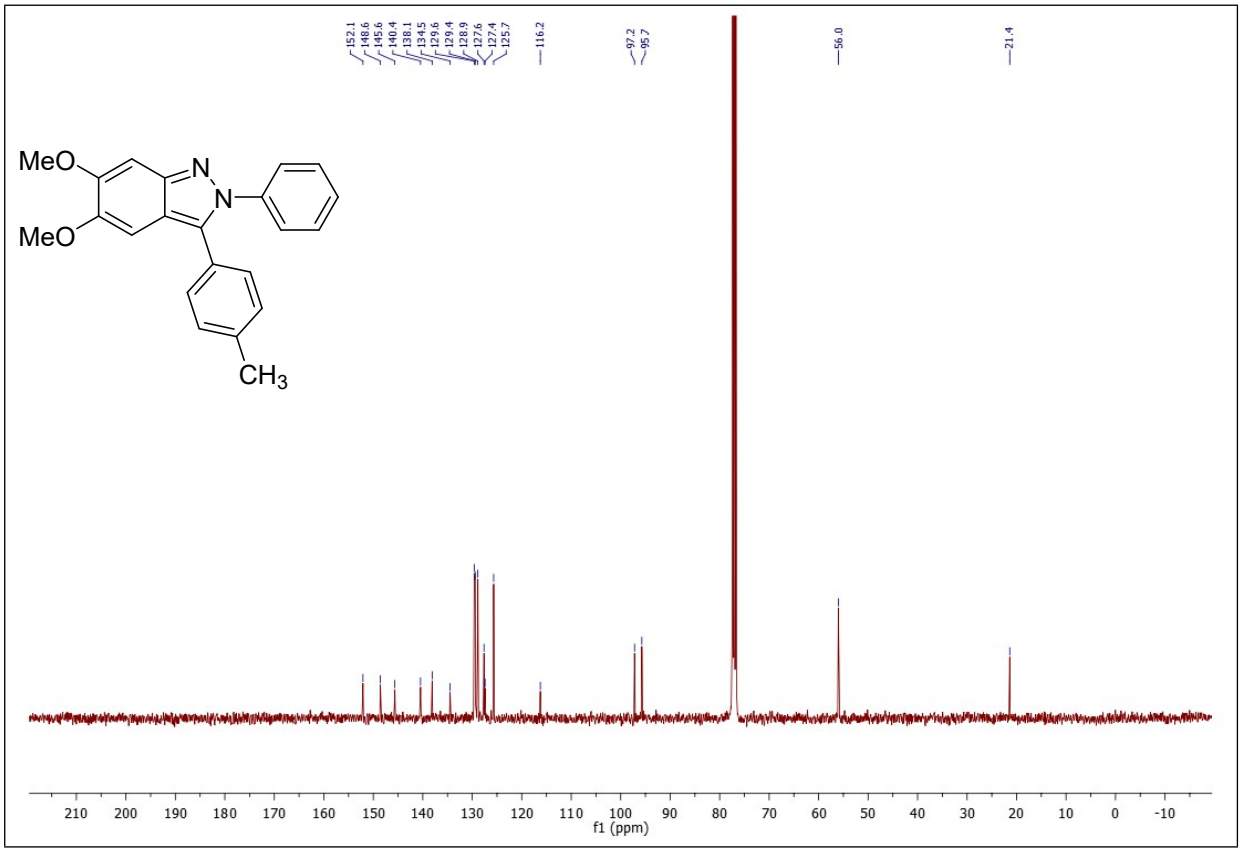
^{19}F NMR spectrum of **3ag** (377 MHz, $CDCl_3$):



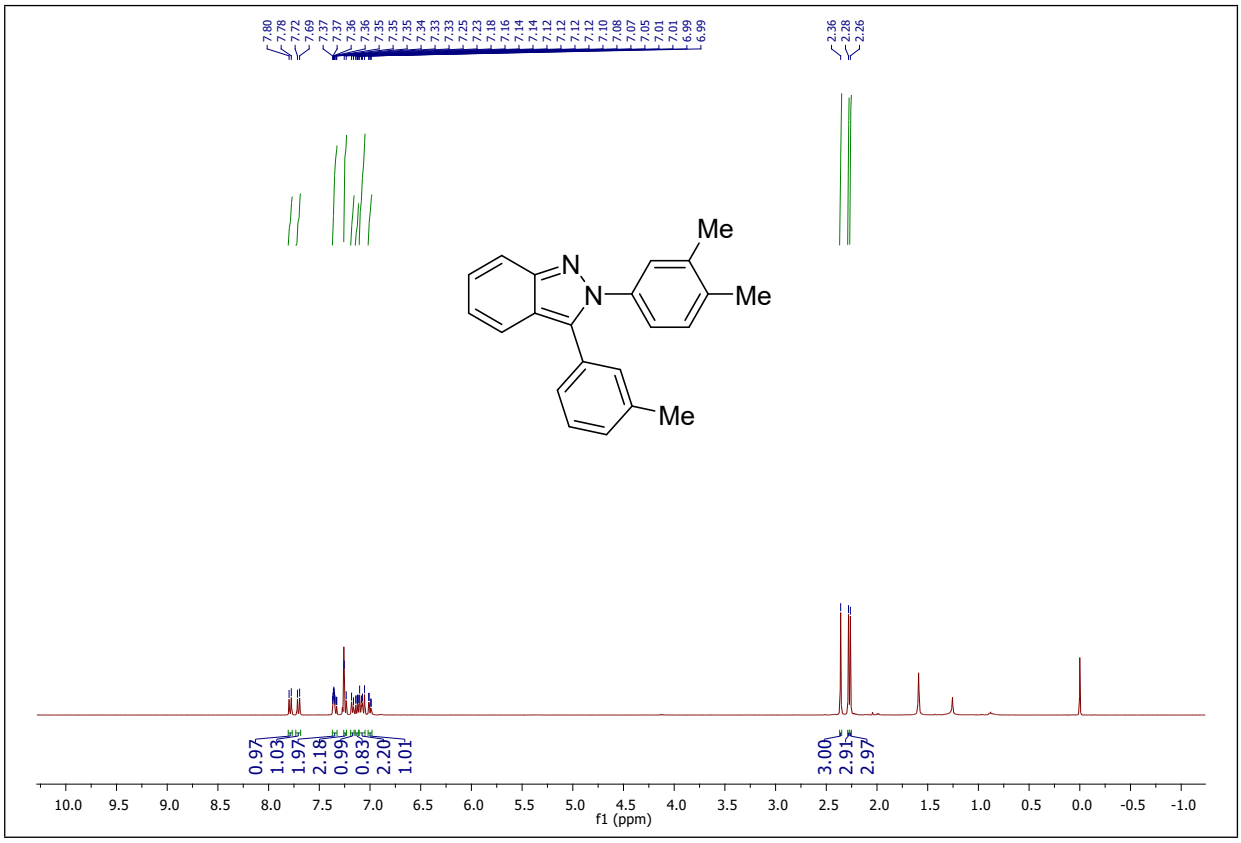
^{1}H NMR spectrum of **3ih** (400 MHz, $CDCl_3$):



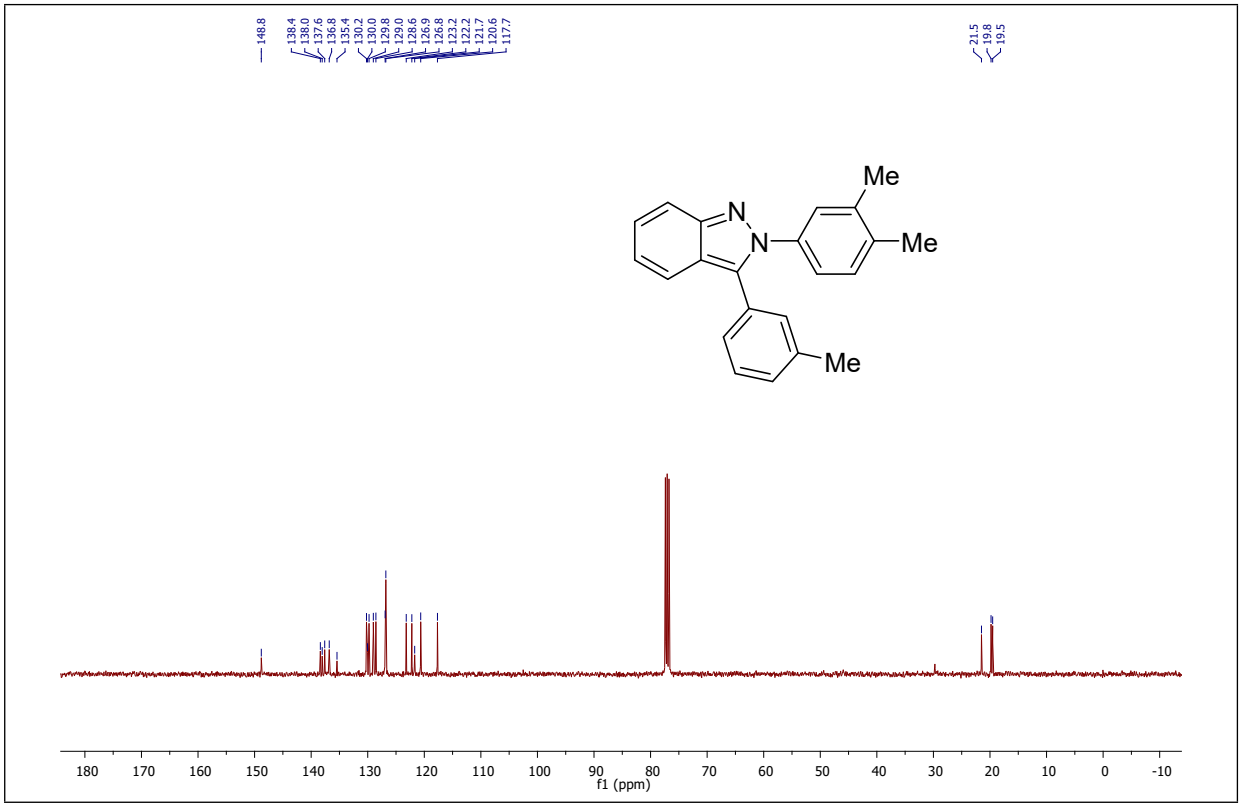
^{13}C NMR spectrum of **3ih** (101 MHz, $CDCl_3$):



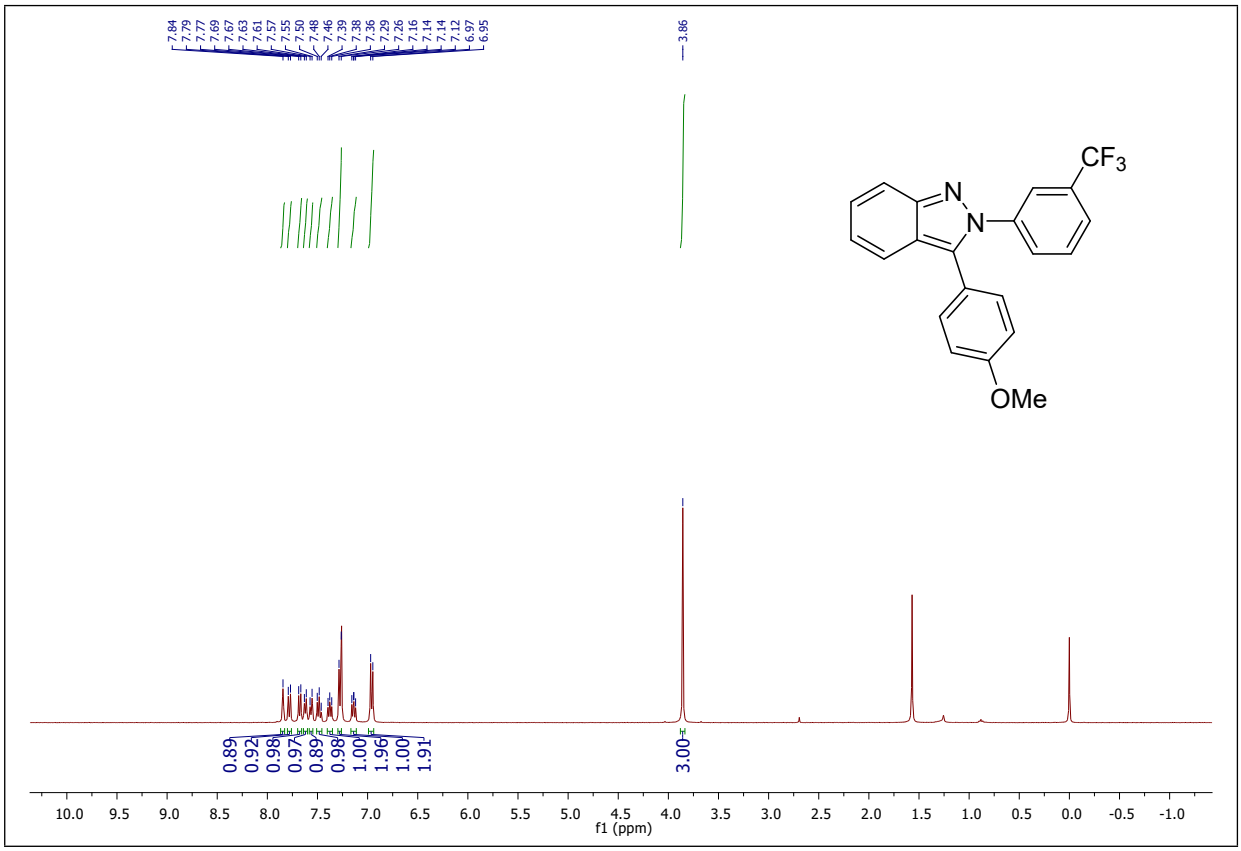
^{1}H NMR spectrum of **3cc** (400 MHz, $CDCl_3$):



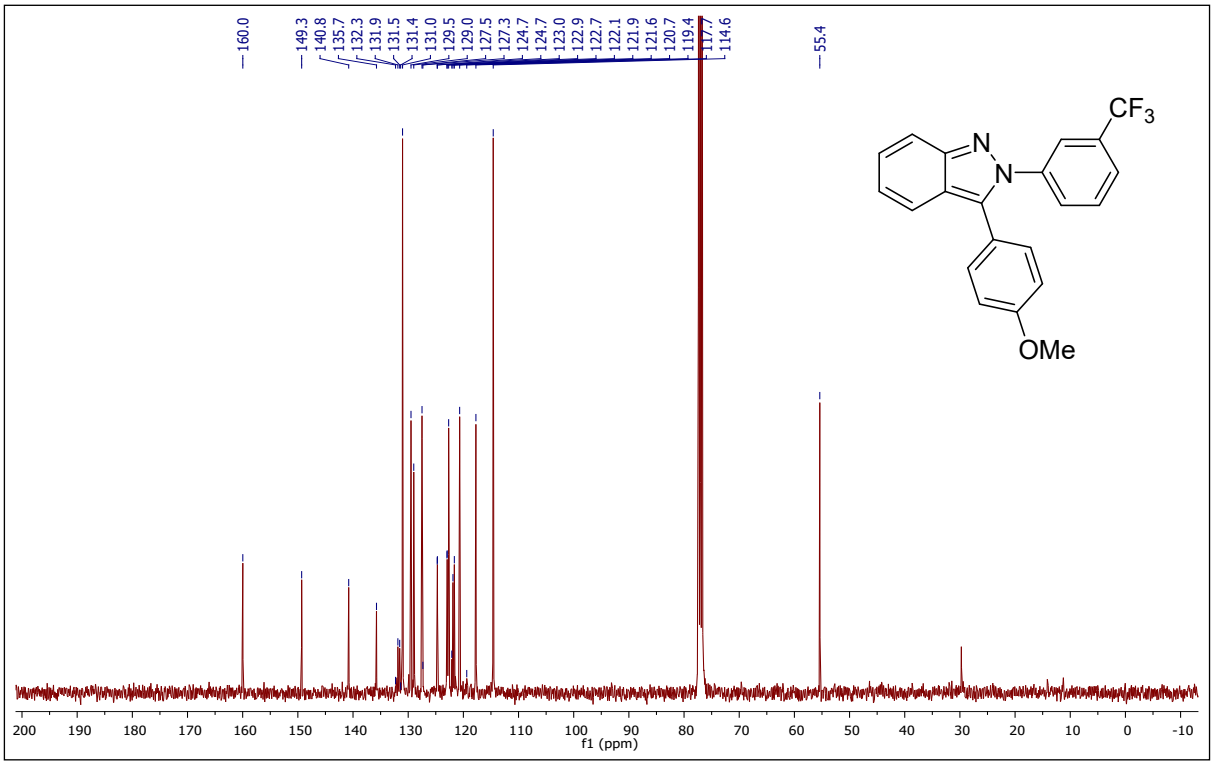
^{13}C NMR spectrum of **3cc** (101 MHz, $CDCl_3$):



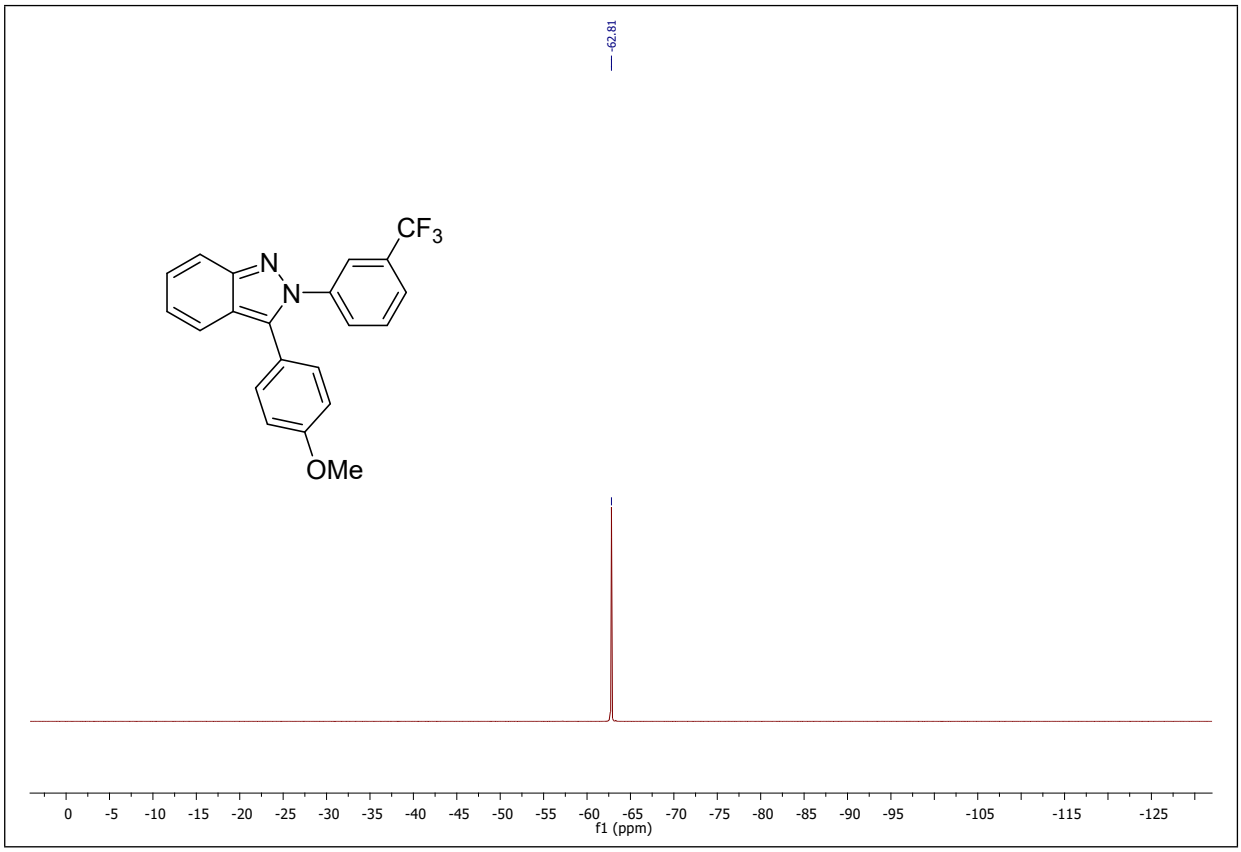
^{1}H NMR spectrum of **3jb** (400 MHz, $CDCl_3$):



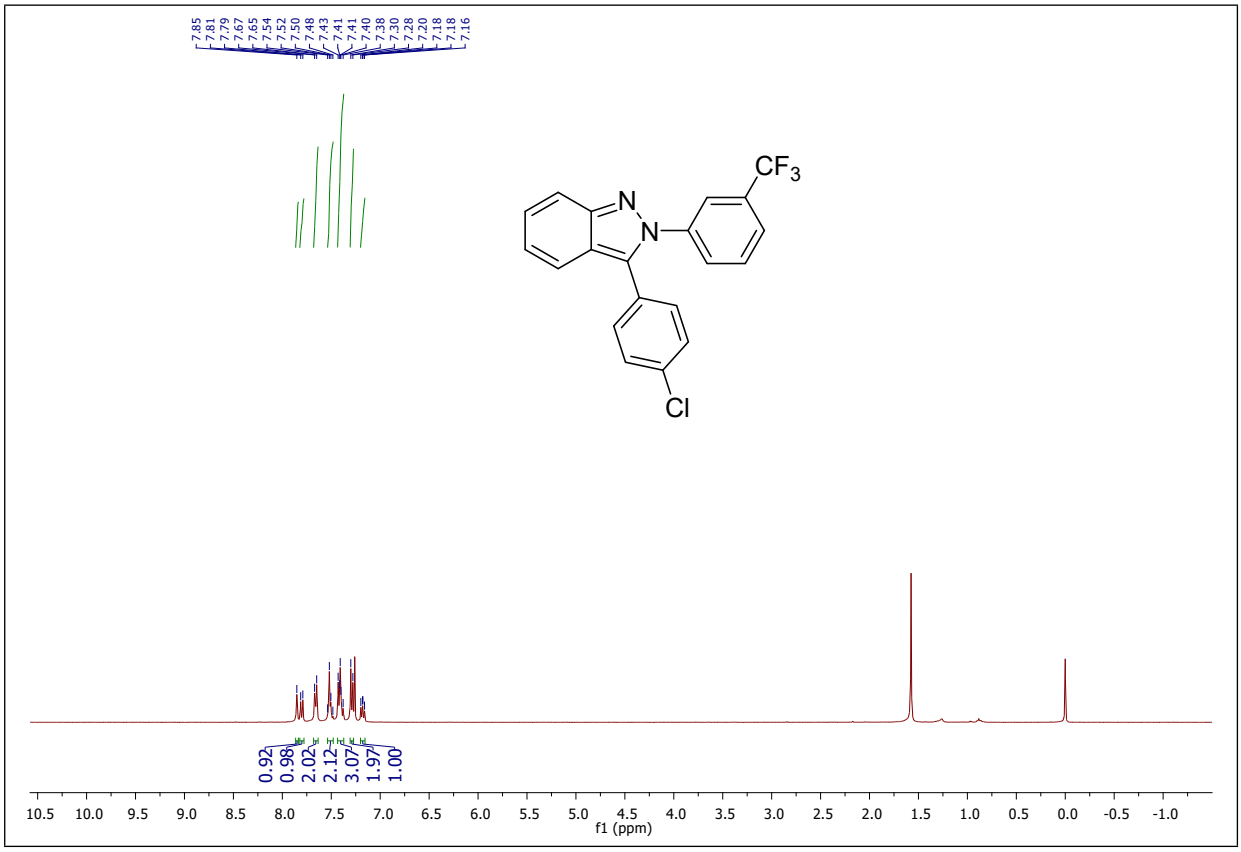
^{13}C NMR spectrum of **3jb** (101 MHz, $CDCl_3$):



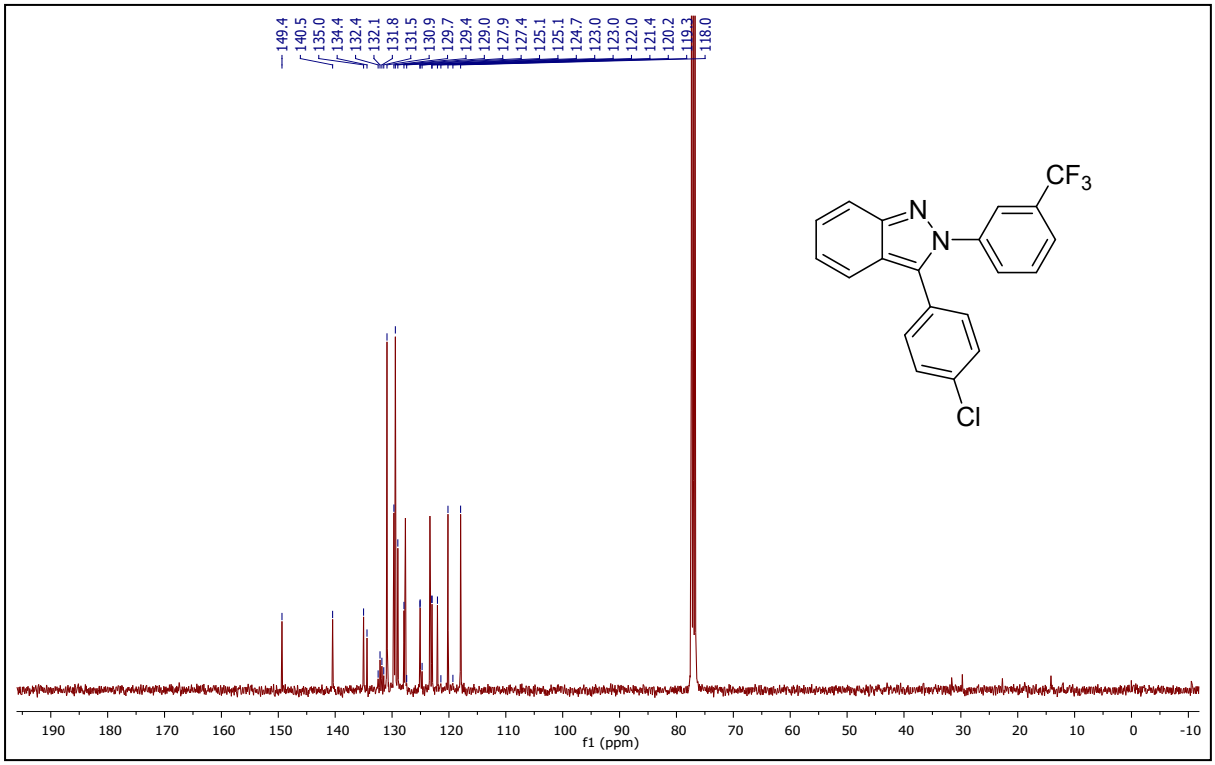
^{19}F NMR spectrum of **3jb** (377 MHz, $CDCl_3$):



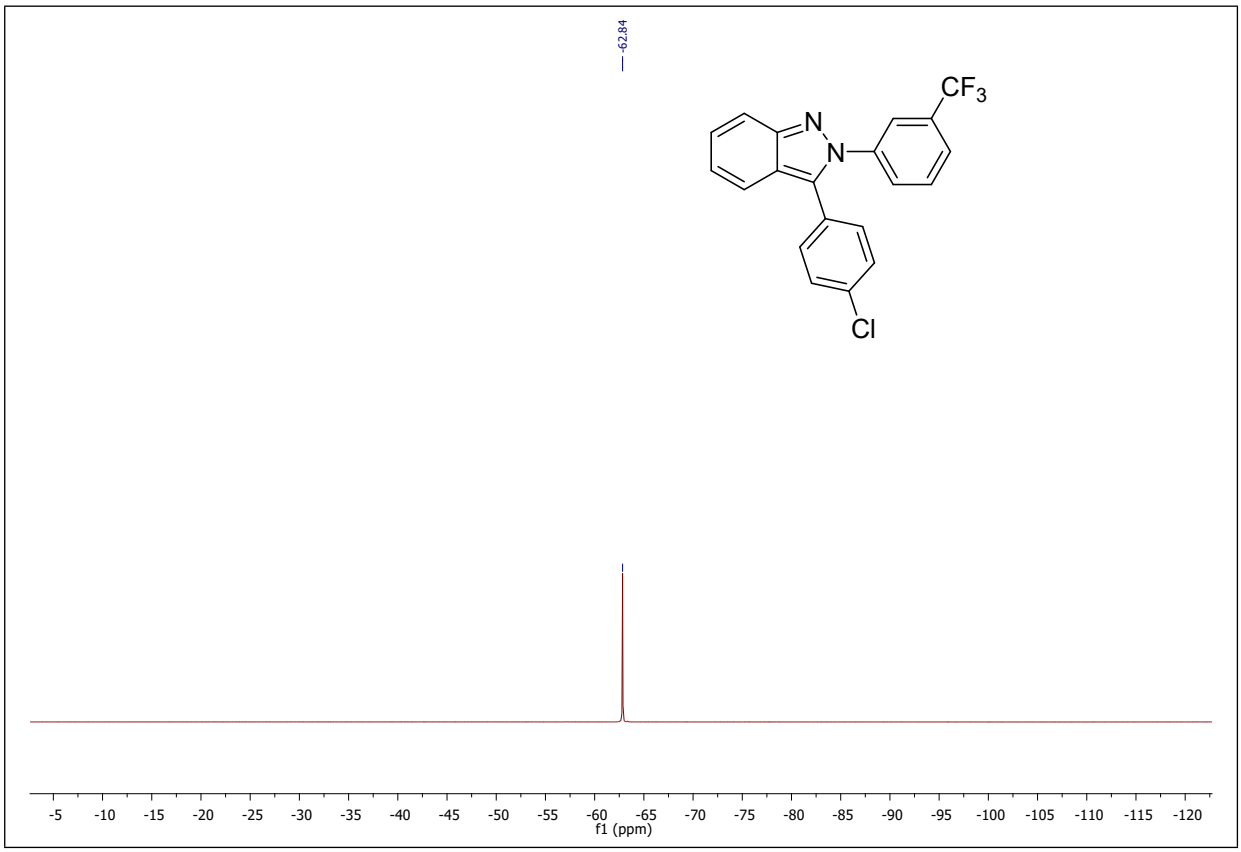
^{1}H NMR spectrum of **3jk** (400 MHz, $CDCl_3$):



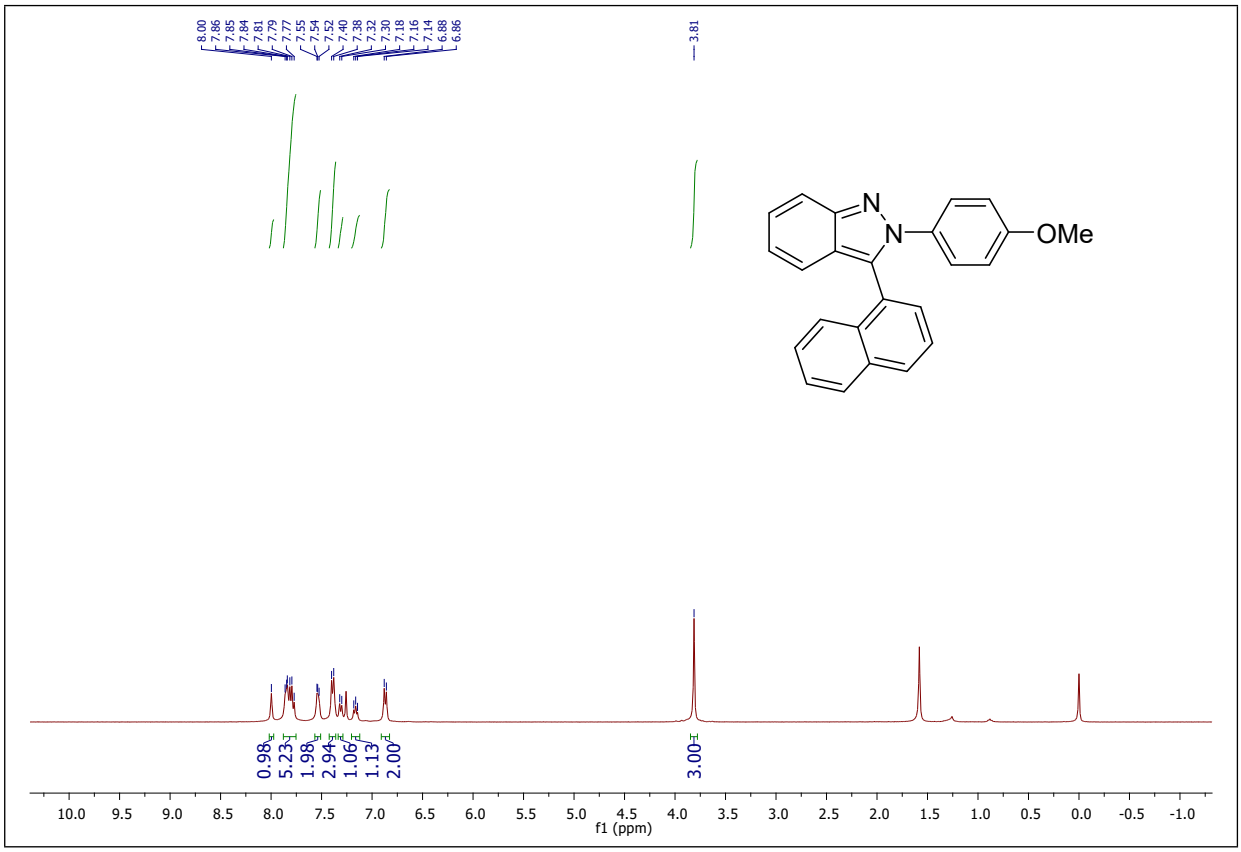
^{13}C NMR spectrum of **3jk** (101 MHz, $CDCl_3$):



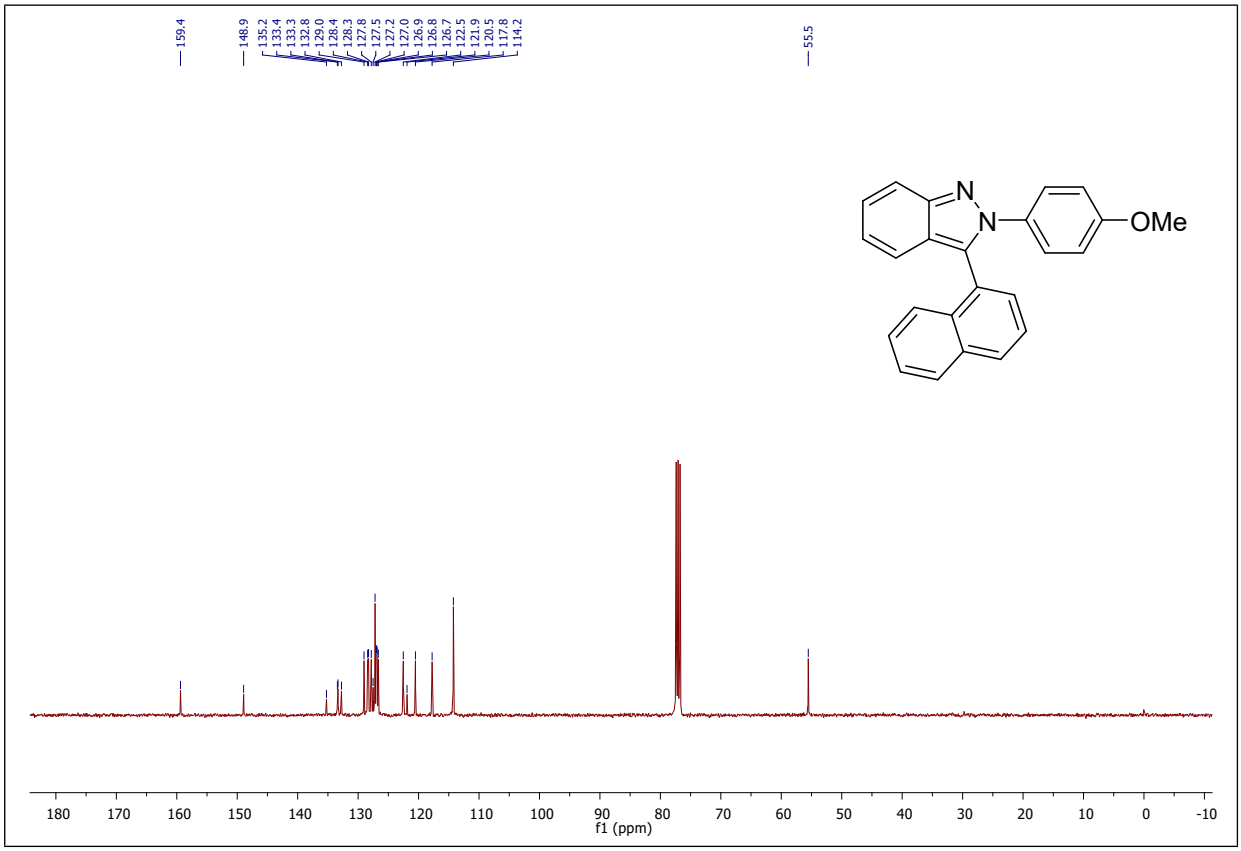
^{19}F NMR spectrum of **3jk** (377 MHz, $CDCl_3$):



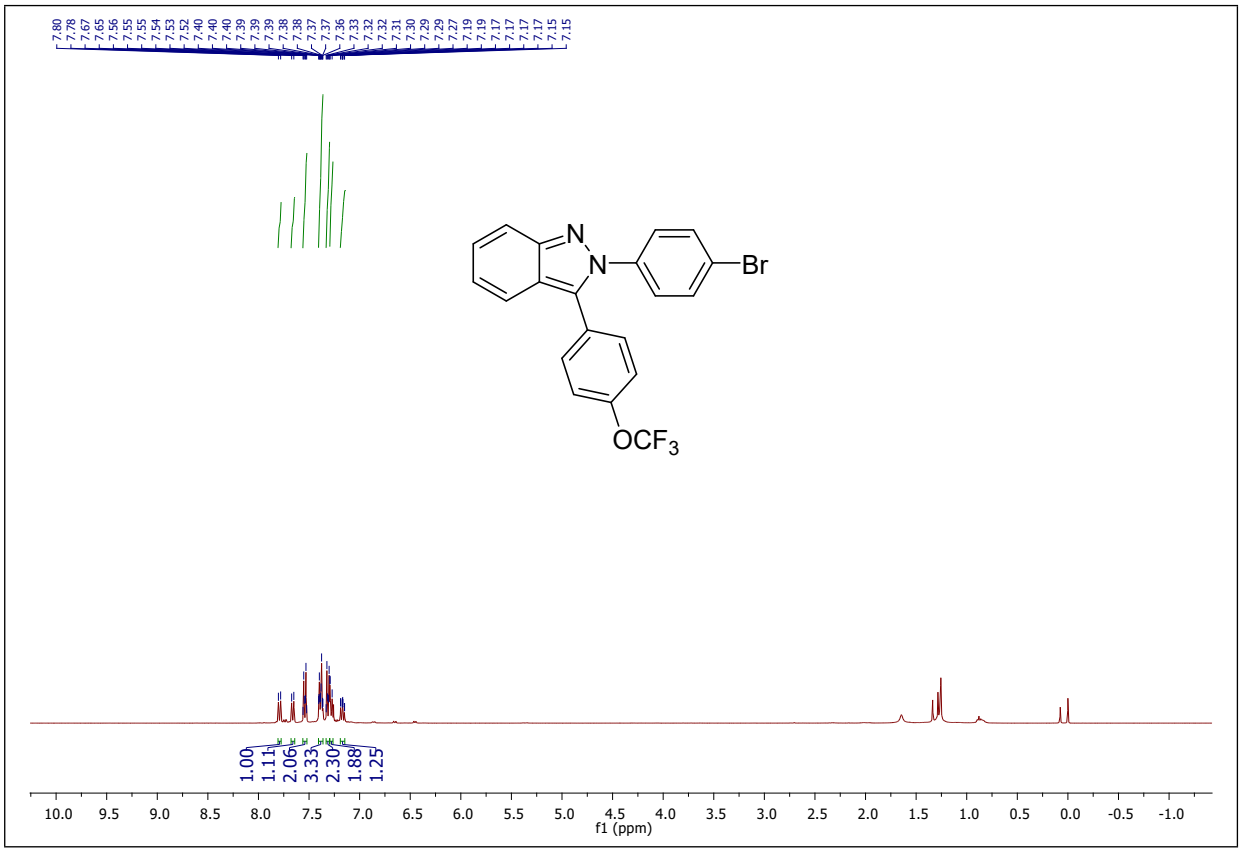
^{1}H NMR spectrum of **3ff** (400 MHz, $CDCl_3$):



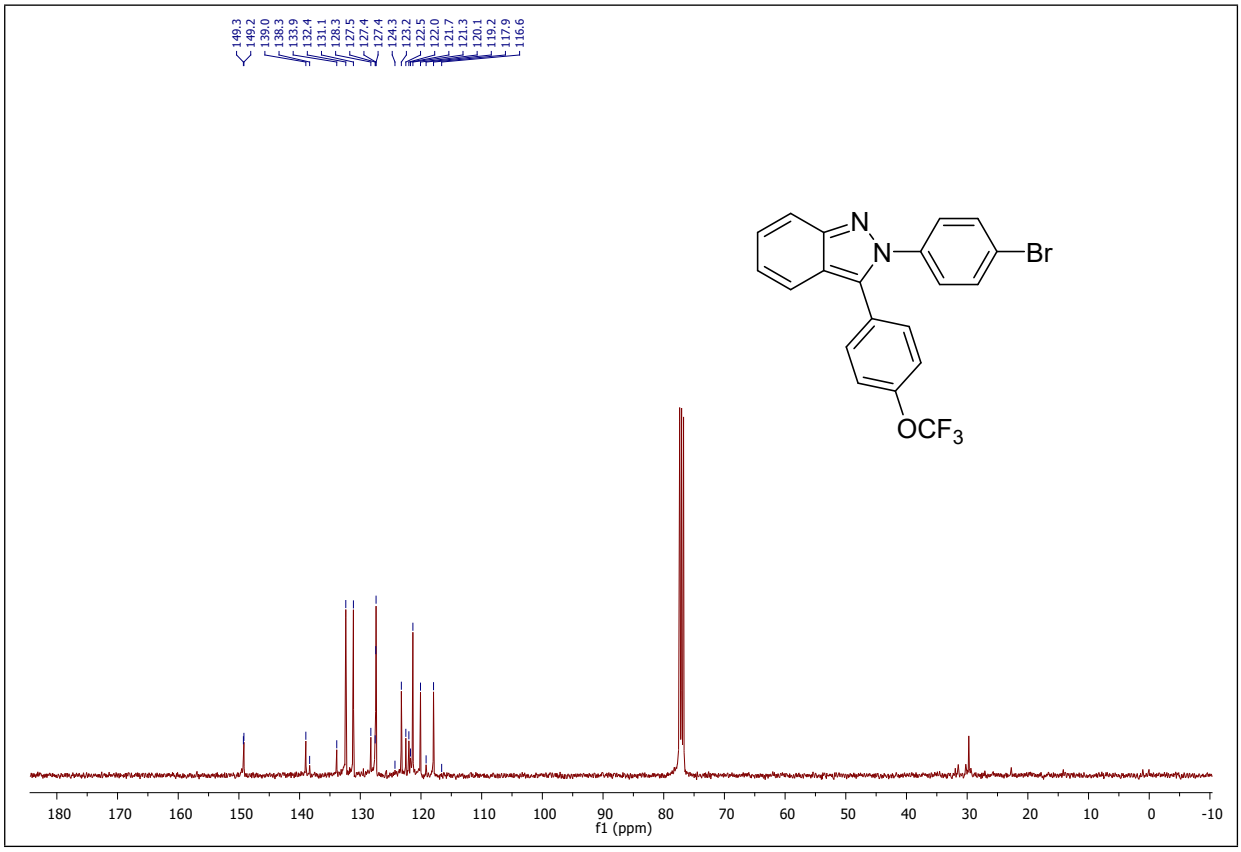
^{13}C NMR spectrum of **3ff** (101 MHz, $CDCl_3$):



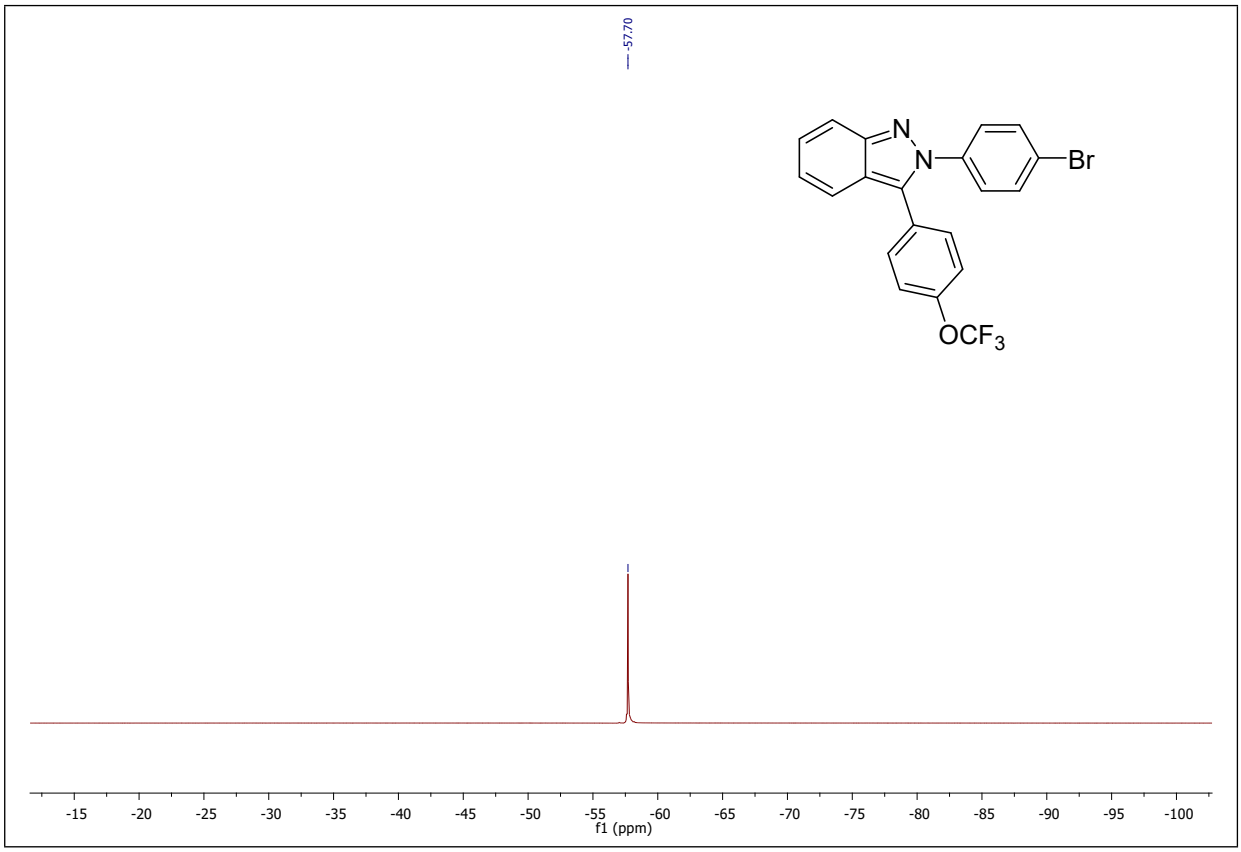
^{1}H NMR spectrum of **3ke** (400 MHz, $CDCl_3$):



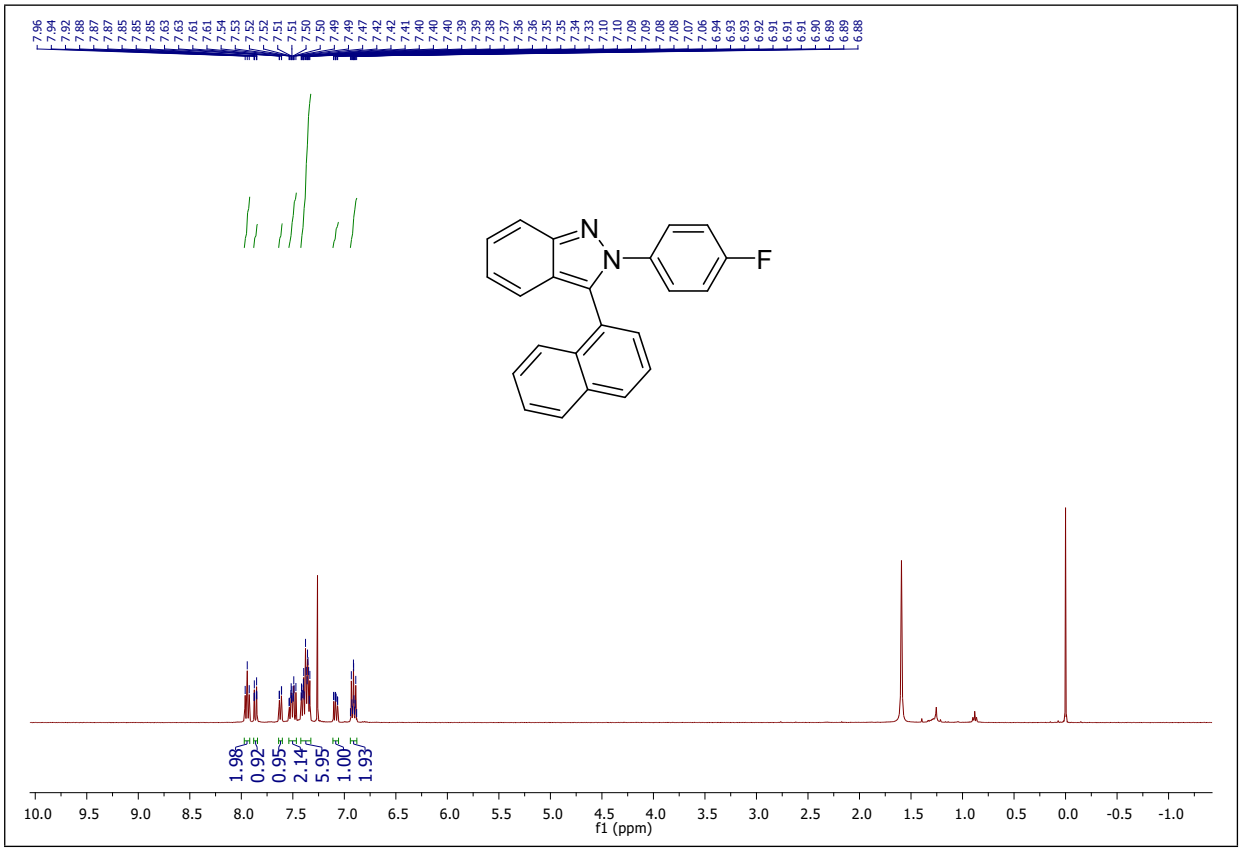
^{13}C NMR spectrum of **3ke** (101 MHz, $CDCl_3$):



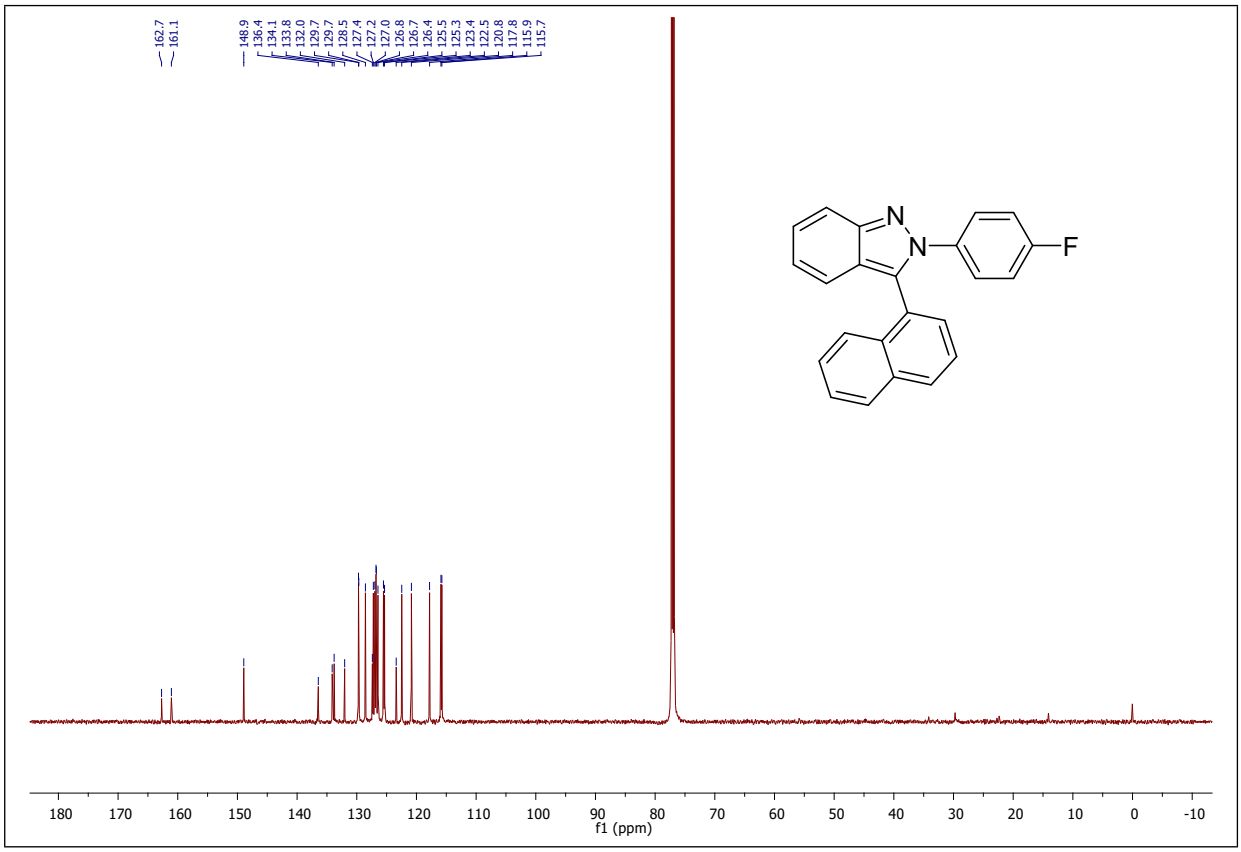
^{19}F NMR spectrum of **3ke** (376 MHz, $CDCl_3$):



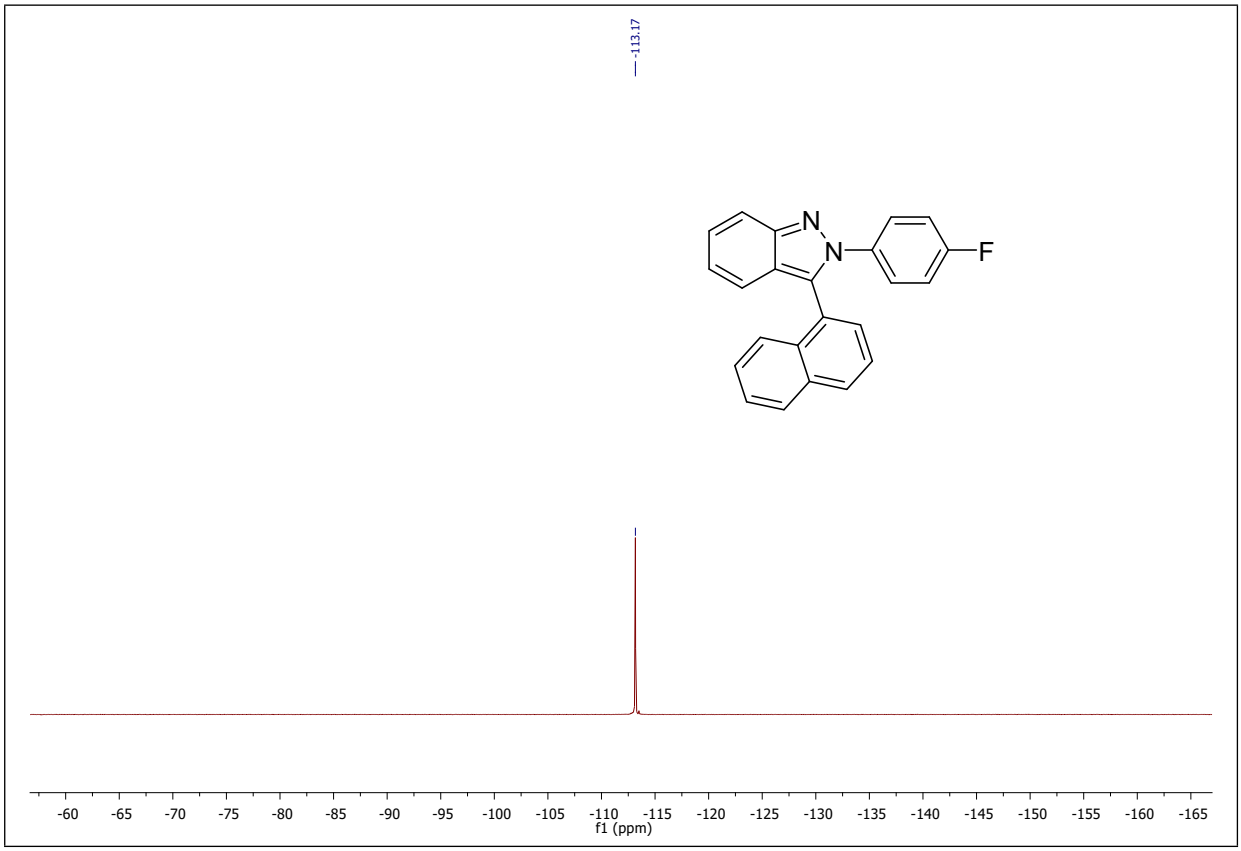
^{1}H NMR spectrum of **3lf** (400 MHz, $CDCl_3$):



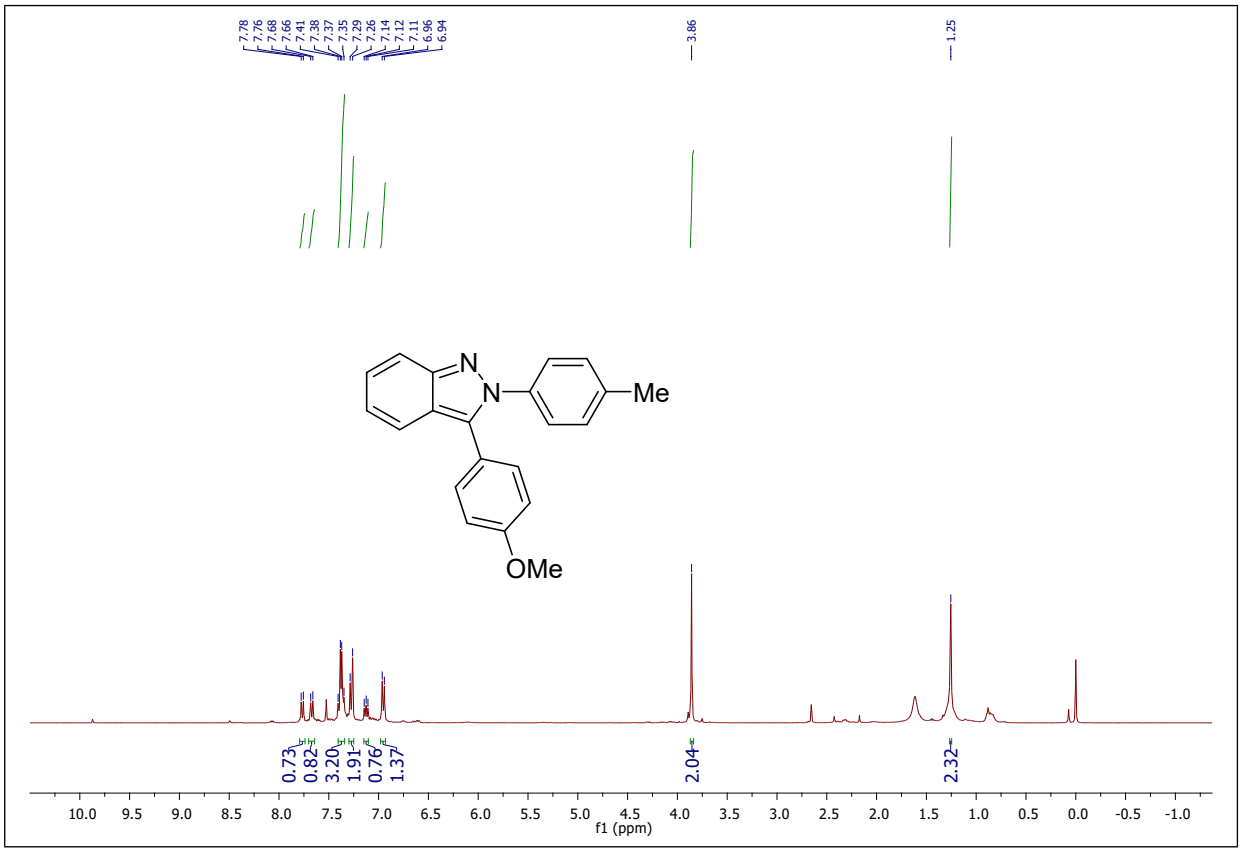
^{13}C NMR spectrum of **3lf** (101 MHz, $CDCl_3$):



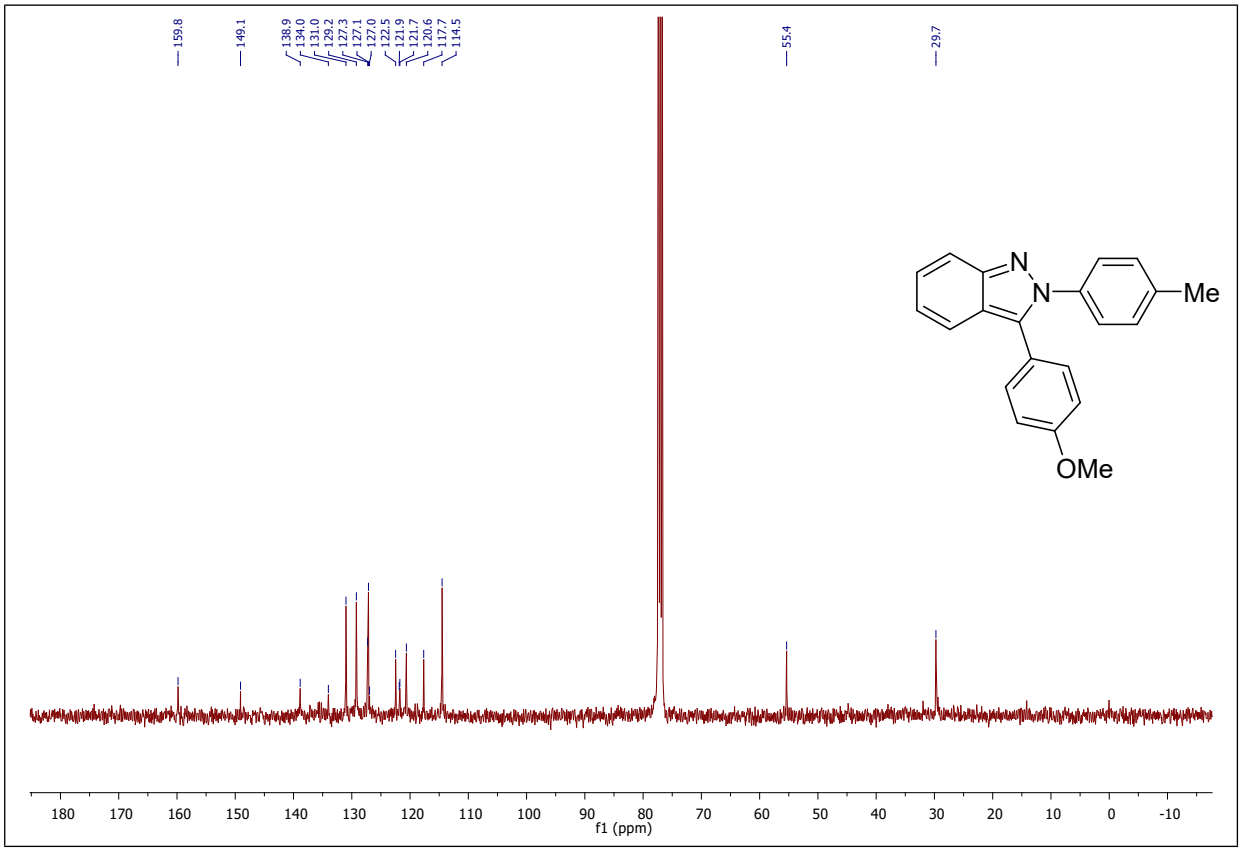
^{19}F NMR spectrum of **3lf** (377 MHz, $CDCl_3$):



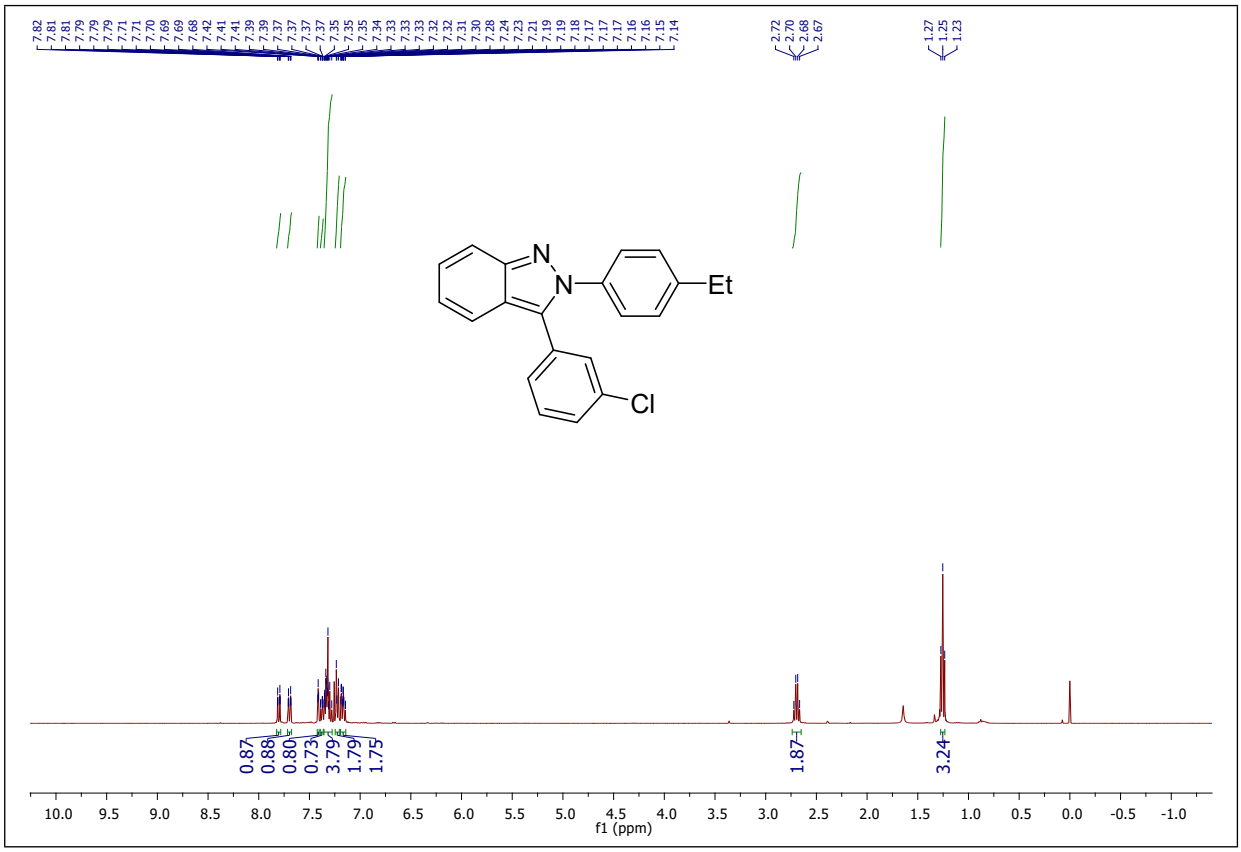
^{1}H NMR spectrum of **3mb** (400 MHz, $CDCl_3$):



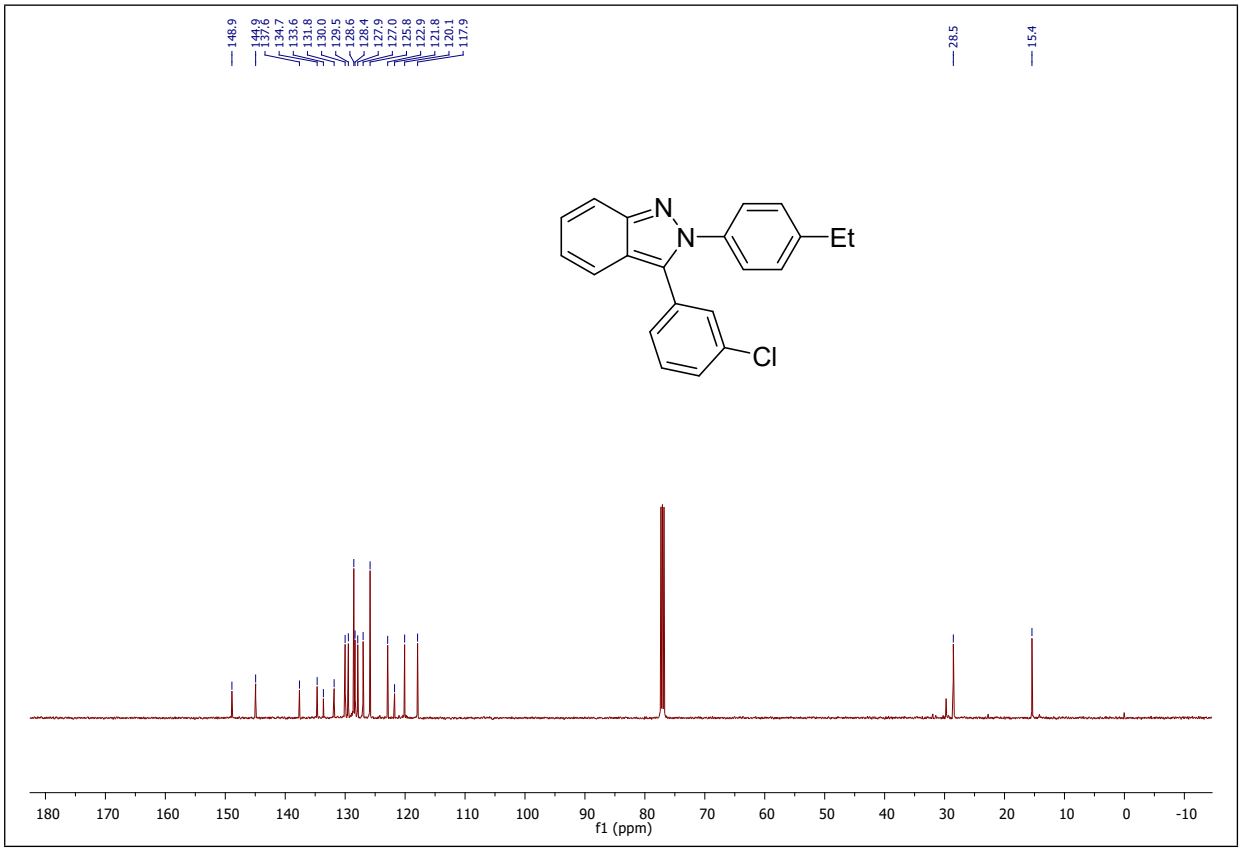
^{13}C NMR spectrum of **3mb** (101 MHz, $CDCl_3$):



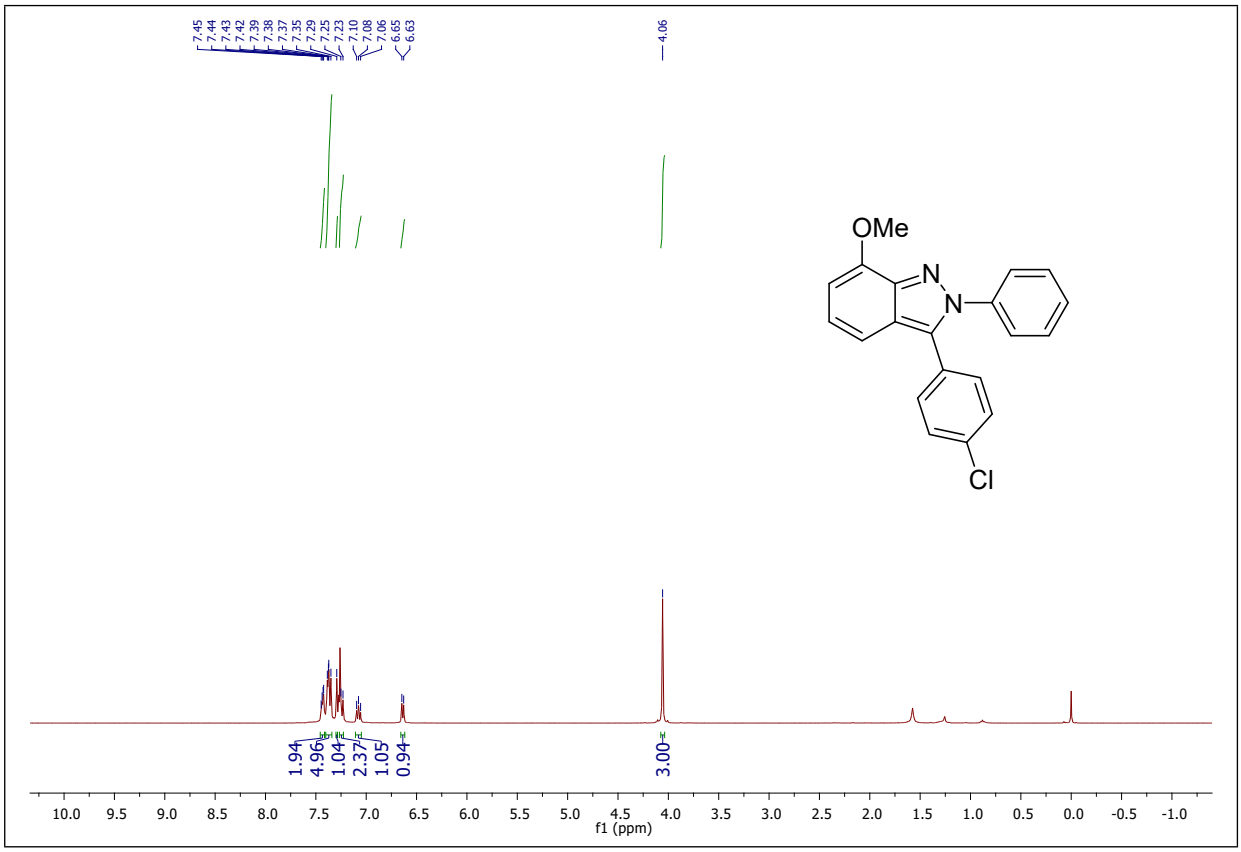
^{1}H NMR spectrum of **3nl** (400 MHz, $CDCl_3$):



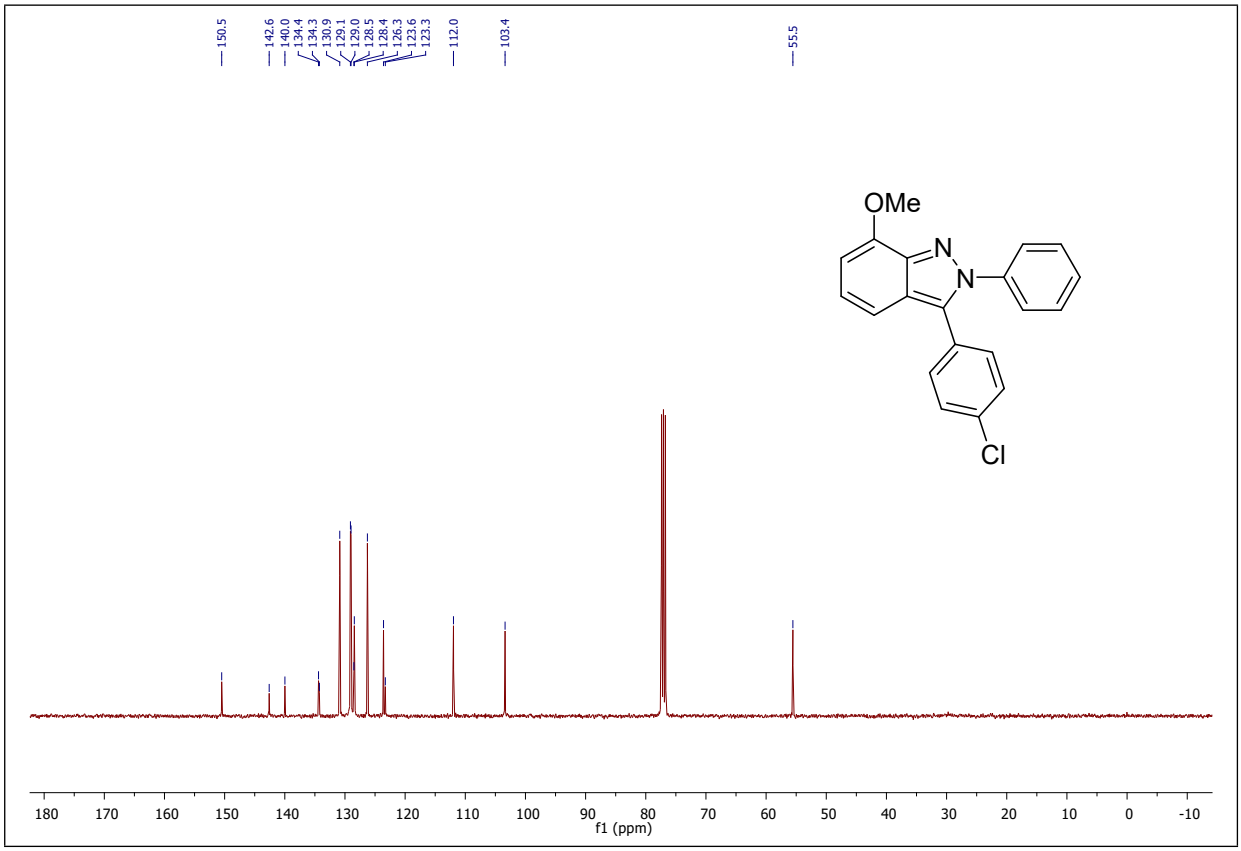
^{13}C NMR spectrum of **3nl** (126 MHz, $CDCl_3$):



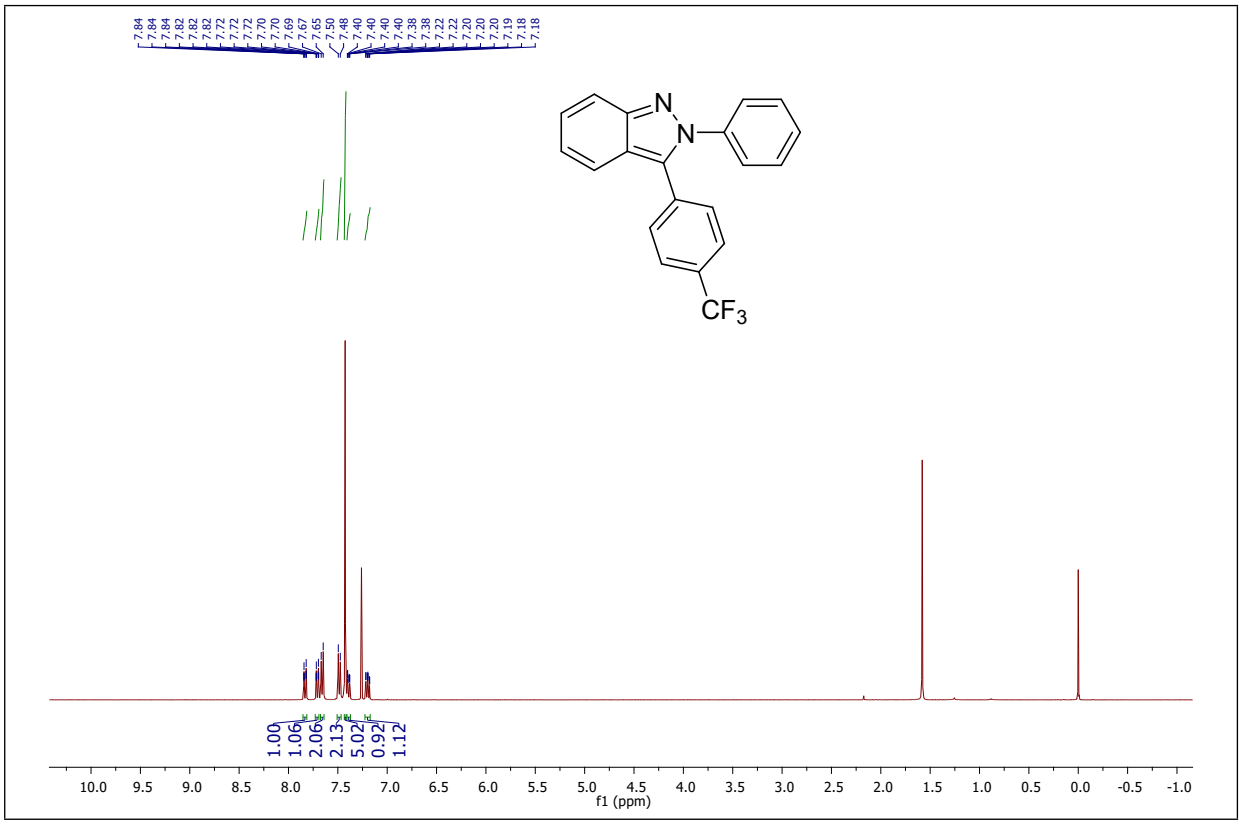
^{1}H NMR spectrum of **3ok** (400 MHz, $CDCl_3$):



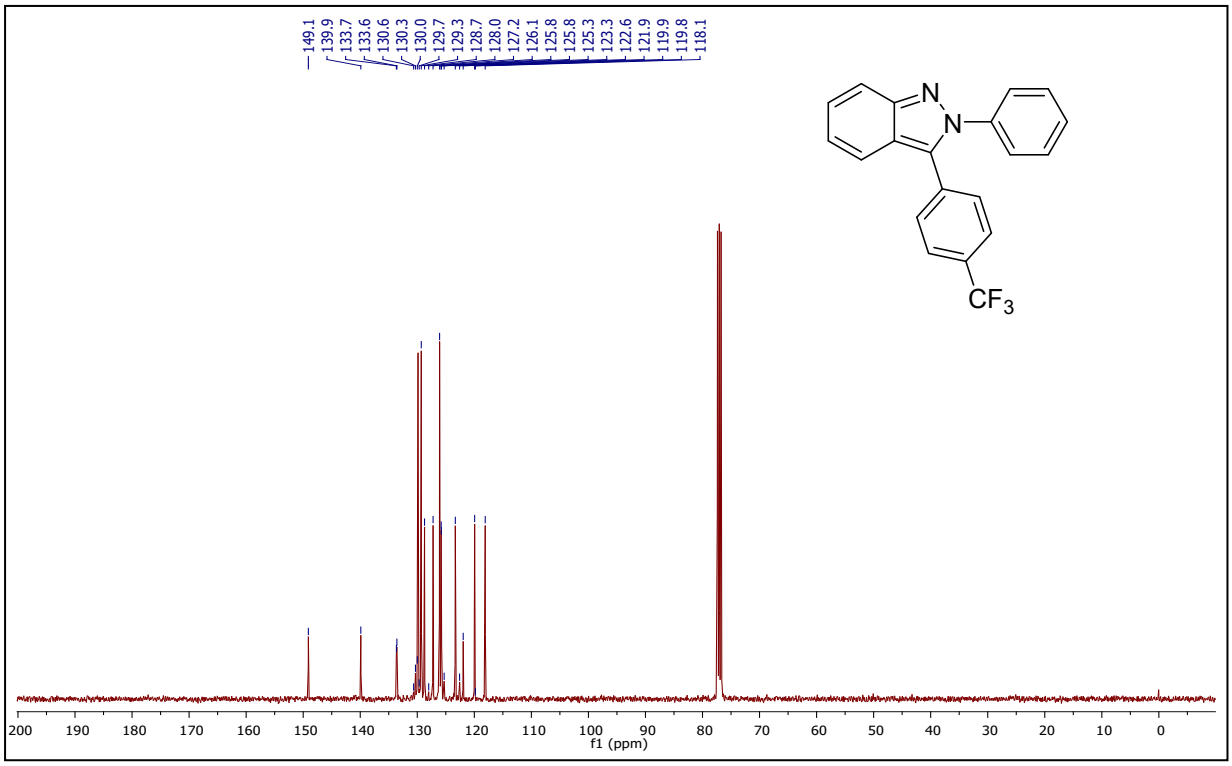
^{13}C NMR spectrum of **3ok** (101 MHz, $CDCl_3$):



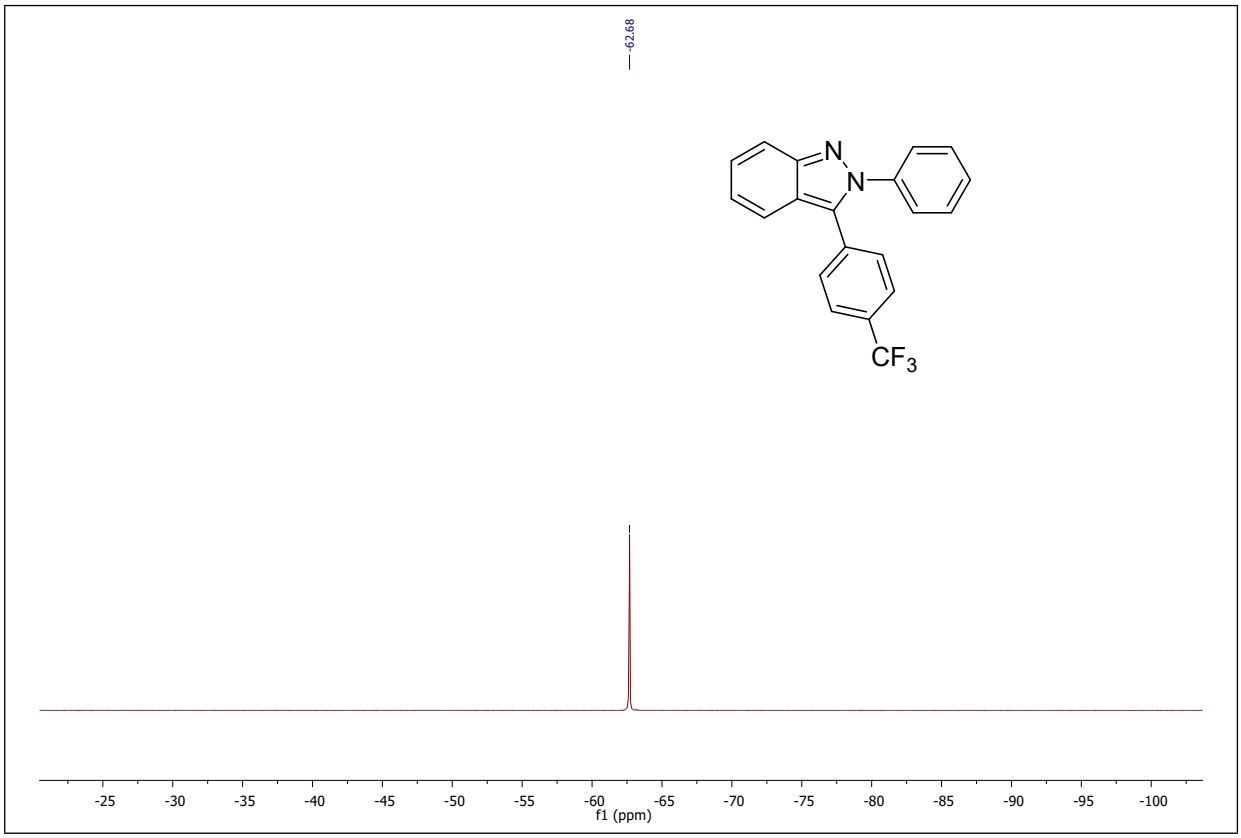
^{1}H NMR spectrum of **3ao** (400 MHz, $CDCl_3$):



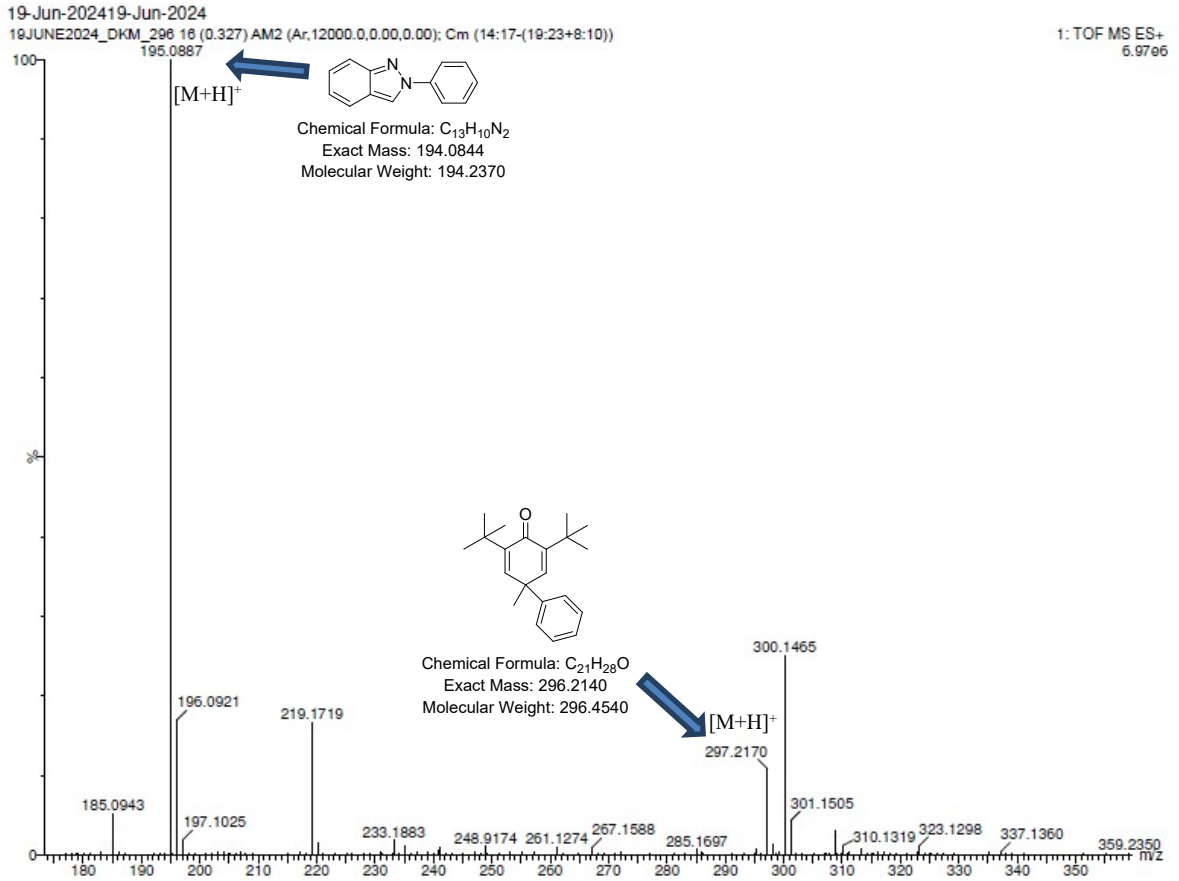
^{13}C NMR spectrum of **3ao** (101 MHz, $CDCl_3$):



^{19}F NMR spectrum of **3ao** (377 MHz, $CDCl_3$):



6. HRMS spectrum of BHT adduct (radical trapping experiment)

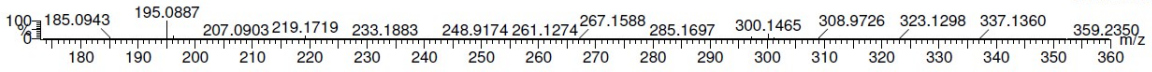


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)
Elements Used:
C: 0-22 H: 0-30 O: 0-1

19-Jun-202419-Jun-2024
19JUNE2024_DKM_296 16 (0.327) AM2 (Ar,12000.0,0.00,0.00); Cm (14:17-(19:23+8:10))
1: TOF MS ES+
6.97e+006



Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
297.2170	297.2218	-4.8	-16.1	7.5	422.0	n/a	n/a	C21 H29 O

7. X-ray Crystallography

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.[2] The structure was solved using intrinsic phasing method[2] and further refined with the SHELXL[3] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms]. Crystal structure determination of [KB1241_0m] Crystal Data for $C_{20}H_{12}N_2F_3Cl$ (M =372.77 g/mol): triclinic, space group P-1 (no. 2), a = 8.0128(15) Å, b = 8.4383(15) Å, c = 13.914(2) Å, α = 94.303(6)°, β = 104.688(6)°, γ = 103.692(7)°, V = 875.0(3) Å 3, Z = 2, T = 294.15 K, μ(MoKα) = 0.254 mm - 1 , Dcalc = 1.415 g/cm^3, 13332 reflections measured (3.058° ≤ 2Θ ≤ 49.992°), 3072 unique (R int = 0.0716, R sigma = 0.0764) which were used in all calculations. The final R 1 was 0.0567 (I > 2σ(I)) and wR 2 was 0.1804 (all data). CCDC 2354212 deposition numbers contain the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/.

8. References

1. M. R. Kumar, A. Park, N. Park, S. Lee, *Org. Lett.* **2011**, *13*(*13*), 3542–3545.
2. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
3. Sheldrick G. M. (2015).ActaCrystallogr C71: 3-8.